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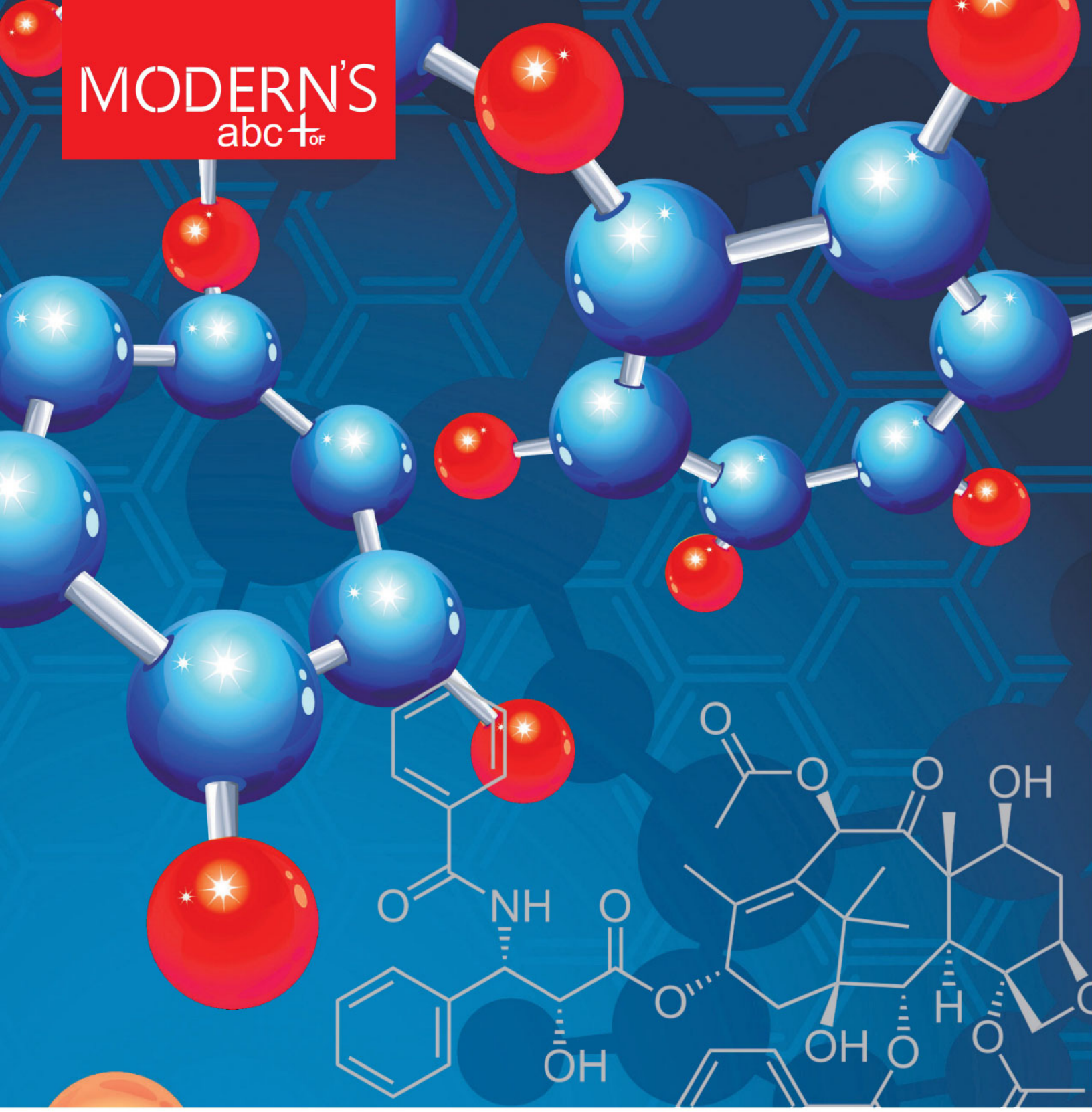

CHEMISTRY

CLASS-XI

PART I & II

STRICTLY ACCORDING TO THE NEW SYLLABUS

INDIA'S FIRST SMART BOOK

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Dr. S.P. Jauhar

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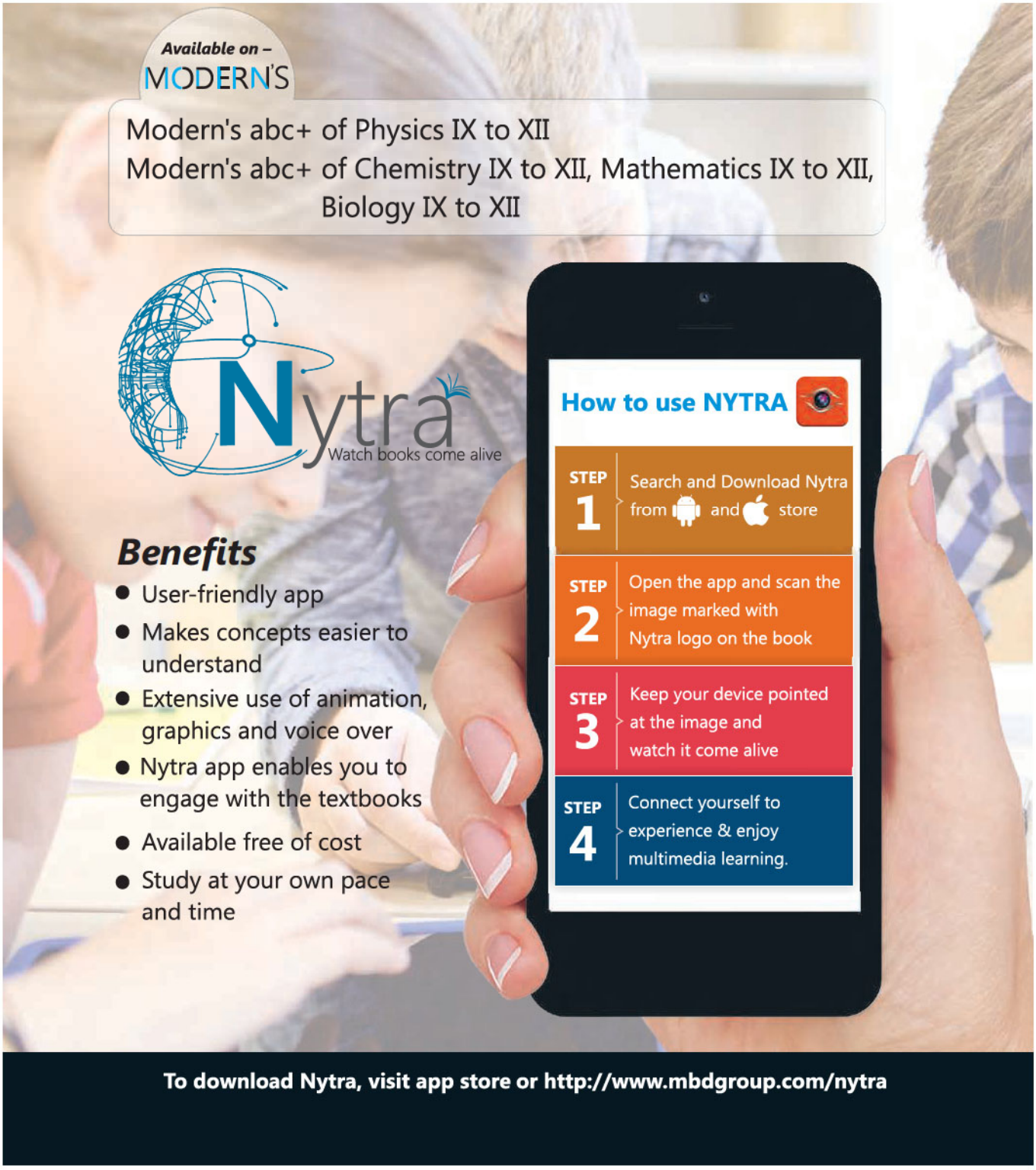

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MODERN'S abc+ OF

CHEMISTRY

INDIA'S FIRST SMART BOOK

Strictly in accordance with the Latest Guidelines and Syllabus issued by N.C.E.R.T. / C.B.S.E.

For Class XI

PART-I

By
Dr. S.P. JAUHAR
Formerly Professor of Chemistry
Department of Chemistry
Panjab University, **Chandigarh**

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REVISED AND UPDATED EDITION 2019-2020

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Published by : **Balwant Sharma**
MODERN PUBLISHERS
MBD House, Railway Road, Jalandhar

Printed at : **M. GULAB SINGH & SONS**
B-5/14, Site IV, Industrial Area Sahibabad (U.P.)

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Preface & Acknowledgement

I feel pleasure in presenting the revised and updated edition of our book "Modern's abc + of Chemistry" for Class XI students. The book has been prepared strictly according to the new syllabus proposed by C.B.S.E. New Delhi and Education Board of other Indian States and N.C.E.R.T. Text Book.

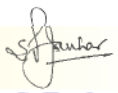
Salient Features of the Book

- Text matter has been planned giving emphasis on fundamental concepts in a simple, clear and systematic method.
- The text has been presented in an interesting style with a large number of Illustrative examples and Numerical problems.
- Additional information about the topic is given in Key Note, Key Facts, Facts File, Learning Plus, In focus to provide stimulus to find more about the subject.
- All the N.C.E.R.T. Text Book exercieses are covered with hints and ensures in different Section of the chapter.
- A number of problems and Short answer questions have been given under the heading Practice Problems promoting problem solving skills in students.
- A large number of Conceptual Questions (Solved) are given in each chapter.
- Advanced Level Problems with solutions are added to accelerate the potential of the students for SOLVING NUMERICAL PROBLEMS for JEE (Advanced).
- All the numerical problems of Practice Problems are completely solved in solution file at the end of each chapter.
- Large number of Numerical Problems from I.I.T., Roorkee, M.L.N.R. and other Competitive Examinations have been given in Competition File.
- Objective questions of various types from previous years' AIPMT/NEET, AIEEE/JEE-Main (online* and offline), IIT JEE/JEE Advanced have been incorporated in Competition file.
- A variety of Multiple Choice Questions from different competitive examinations have been added to make the book useful for the preparation of competitive examinations in Competition File.
- MCQs with more than one correct answers and MCQs based on given comprehension/passage according to latest IIT pattern are also given.
- Objective Questions in the form of assertion-reason type are also given.
- At the end of each chapter, Quick Revision through Objective Questions "Quick Memory Test" have been added to check the retention power of the students.
- A number of Higher Order Thinking Skills (HOTS) and Advanced Level with answers are included at the end of each chapter.
- The definition of Key Terms &Laws and QUICK CHAPTER ROUND UP are given at the end under the heading Chapter Summary.
- UNIT PRACTICE TESTS with Hints & Solutions are given at the end of each chapter to help the students to check their performance after covering the chapter. A Mock Test with solutions according to CBSE pattern is given at the end of the book.

I am extremely thankful to many teachers and students who have been sending their valuable suggestions and comments for the improvement of the book. I am greatly indebted to them. I wish to acknowledge my sincere thanks to Dr. (Mrs.) Sheenu Jauhar for her untiring efforts and valuable contribution in critical revision of the book and updating Objective Questions. I also feel pleasure to express my thanks to Mr. Arun Kamboj (G.S.S. School, Tohana), Dr. G. J. P. Singh (Chemistry Deptt., P.U., Chandigarh), Dr. Sajeev Soni (S.D. College, Chandigarh), Dr. A.N. Sharma (Govt. College, Hamirpur), Ms. Parveen (Faridkot), Mrs. Anju Goel (Govt. S. S. School Sec. 16, Chandigarh), Dr. O.P. Sood, Dr. G.S. Arora, Mrs. Sunita Saroha (D.A.V. S.S. School, Sec. 15, Chandigarh, Mr. Gaurav Chakraborty, Mrs. Amita Sharma (Saraswati Institute, Chandigarh), Mrs. Seema (Seema Chemistry classes), Mr. Sudhanshu Jaitley (Chandigarh), Mr. Deepak Mishra (H.O.D. Shri Gauri Shankar Inter College, Ferozabad), Mr. Praveen Kumar (S.V.M. Senior Sec. School, Kosi Kalan, Mathura), Mr. Vikas Chander (Saint Mary S.S. School Gurdaspur), Shri Rakesh Jassotia, (Sr. Lecturer, Govt. G.H.S.S. Nagari PAROLE, Kathua) and Mr. Vaibhav Yavlekar (Ujjain. I am also highly thankful to Mr. Vinod Kumar Jangra (G.S.S.S. Akbarpur Baroto, Sonepat) and Dr. Anjul Rajput (Dhampur) for thoroughly checking of the book and providing valuable suggestions. I am also thankful to Ms. Arshdeep for her sincere and dedicated editorial work. Finally, I am happy to express my sincerest thanks and indebtness to our dynamic and versatile publisher and his efficient staff for making the project successful. I am also thankful to Mr. Manik Juneja, Director — Content and Production, Mr. B.S. Rawat, Mr. S.K. Sikka, Mr. Ravinder Pathania and L.B. Mishra who have taken great pains in bringing up the book.

I would also like to gratefully appreciate the tremendous and valuable efforts of Mr. Manu Jauhar for excellent thoughtful editing of the book.

I hope that the present book will be warmly received by the students and the teachers. Suggestions for the further improvement of the book will be gratefully acknowledged.



– Dr. S.P. Jauhar

* Memory based JEE-Main 2019 online questions are also included.

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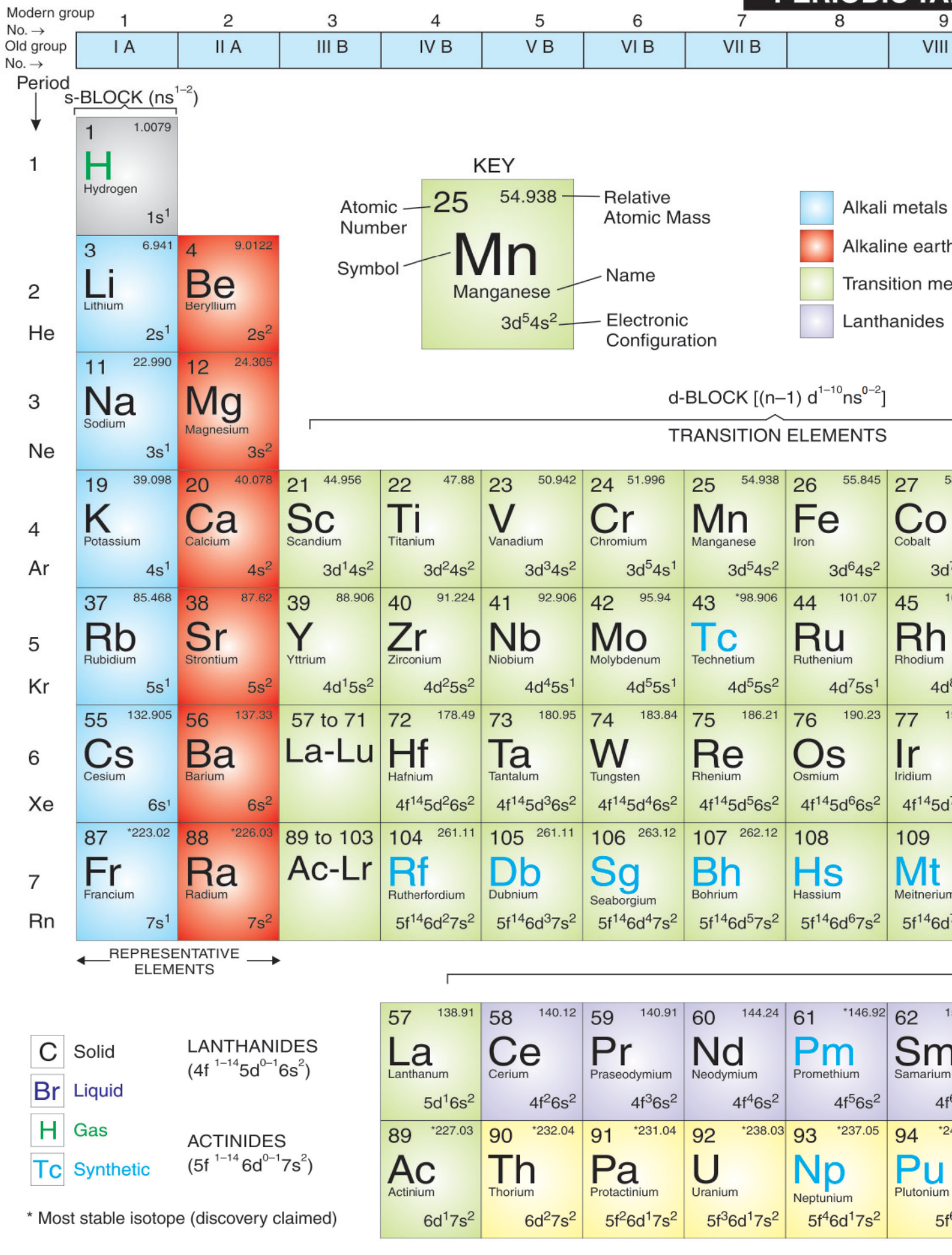
Modern group No. →
Old group No. →
1 2 3 4 5 6 7 8 9
I A II A III B IV B V B VI B VII B VIII
Period
s-BLOCK (ns1–2)
KEY
Atomic Number
25
54.938
Relative Atomic Mass
Mn
Symbol
Manganese
Name
3d54s2
Electronic Configuration
Alkali metals
Alkaline earth
Transition me
Lanthanides
d-BLOCK [(n–1) d1–10ns0–2]
TRANSITION ELEMENTS
1 1.0079 H Hydrogen 1s1
3 6.941 Li Lithium 2s1
4 9.0122 Be Beryllium 2s2
11 22.990 Na Sodium 3s1
12 24.305 Mg Magnesium 3s2
19 39.098 K Potassium 4s1
20 40.078 Ca Calcium 4s2
21 44.956 Sc Scandium 3d14s2
22 47.88 Ti Titanium 3d24s2
23 50.942 V Vanadium 3d34s2
24 51.996 Cr Chromium 3d54s1
25 54.938 Mn Manganese 3d54s2
26 55.845 Fe Iron 3d64s2
27 5 Co Cobalt 3d
37 85.468 Rb Rubidium 5s1
38 87.62 Sr Strontium 5s2
39 88.906 Y Yttrium 4d15s2
40 91.224 Zr Zirconium 4d25s2
41 92.906 Nb Niobium 4d45s1
42 95.94 Mo Molybdenum 4d55s1
43 *98.906 Tc Technetium 4d55s2
44 101.07 Ru Ruthenium 4d75s1
45 1 Rh Rhodium 4d
55 132.905 Cs Cesium 6s1
56 137.33 Ba Barium 6s2
57 to 71 La-Lu
72 178.49 Hf Hafnium 4f145d26s2
73 180.95 Ta Tantalum 4f145d36s2
74 183.84 W Tungsten 4f145d46s2
75 186.21 Re Rhenium 4f145d56s2
76 190.23 Os Osmium 4f145d66s2
77 1 Ir Iridium 4f145d
87 *223.02 Fr Francium 7s1
88 *226.03 Ra Radium 7s2
89 to 103 Ac-Lr
104 261.11 Rf Rutherfordium 5f146d27s2
105 261.11 Db Dubnium 5f146d37s2
106 263.12 Sg Seaborgium 5f146d47s2
107 262.12 Bh Bohrium 5f146d57s2
108 Hs Hassium 5f146d67s2
109 Mt Meitnerium 5f146d
REPRESENTATIVE ELEMENTS
57 138.91 La Lanthanum 5d16s2
58 140.12 Ce Cerium 4f26s2
59 140.91 Pr Praseodymium 4f36s2
60 144.24 Nd Neodymium 4f46s2
61 *146.92 Pm Promethium 4f56s2
62 1 Sm Samarium 4f
89 *227.03 Ac Actinium 6d17s2
90 *232.04 Th Thorium 6d27s2
91 *231.04 Pa Protactinium 5f26d17s2
92 *238.03 U Uranium 5f36d17s2
93 *237.05 Np Neptunium 5f46d17s2
94 *2 Pu Plutonium 5f
C Solid
Br Liquid
H Gas
Tc Synthetic
LANTHANIDES (4f 1–14 5d0–1 6s2)
ACTINIDES (5f 1–14 6d0–1 7s2)
* Most stable isotope (discovery claimed)

ABLE OF THE ELEMENTS

9	10	11	12	13	14	15	16	17	18
I B		I B	II B	III A	IV A	V A	VI A	VII A	VIII A

p – BLOCK (ns^2np^{1-6})

- Actinides
- Other metals
- Non-metals
- Noble gases

									2 4.0026 **He** Helium $1s^2$
				5 10.811 **B** Boron $2s^22p^1$	6 12.011 **C** Carbon $2s^22p^2$	7 14.007 **N** Nitrogen $2s^22p^3$	8 15.999 **O** Oxygen $2s^22p^4$	9 18.998 **F** Fluorine $2s^22p^5$	10 20.18 **Ne** Neon $2s^22p^6$
				13 26.982 **Al** Aluminium $3s^23p^1$	14 28.086 **Si** Silicon $3s^23p^2$	15 30.974 **P** Phosphorus $3s^23p^3$	16 32.066 **S** Sulphur $3s^23p^4$	17 35.453 **Cl** Chlorine $3s^23p^5$	18 39.948 **Ar** Argon $3s^23p^6$
58.933 ... $d^7 4s^2$	28 58.693 **Ni** Nickel $3d^8 4s^2$	29 63.546 **Cu** Copper $3d^{10} 4s^1$	30 65.39 **Zn** Zinc $3d^{10} 4s^2$	31 69.723 **Ga** Gallium $3d^{10} 4s^2 4p^1$	32 72.61 **Ge** Germanium $3d^{10} 4s^2 4p^2$	33 74.992 **As** Arsenic $3d^{10} 4s^2 4p^3$	34 78.96 **Se** Selenium $3d^{10} 4s^2 4p^4$	35 79.904 **Br** Bromine $3d^{10} 4s^2 4p^5$	36 83.80 **Kr** Krypton $3d^{10} 4s^2 4p^6$
102.91 ... $d^8 5s^1$	46 106.42 **Pd** Palladium $4d^{10}$	47 107.87 **Ag** Silver $4d^{10} 5s^1$	48 112.41 **Cd** Cadmium $4d^{10} 5s^2$	49 114.82 **In** Indium $4d^{10} 5s^2 5p^1$	50 118.71 **Sn** Tin $4d^{10} 5s^2 5p^2$	51 121.76 **Sb** Antimony $4d^{10} 5s^2 5p^3$	52 127.60 **Te** Tellurium $4d^{10} 5s^2 5p^4$	53 126.90 **I** Iodine $4d^{10} 5s^2 5p^5$	54 131.29 **Xe** Xenon $4d^{10} 5s^2 5p^6$
192.22 ... $d^7 6s^2$	78 195.08 **Pt** Platinum $4f^{14} 5d^9 6s^1$	79 196.97 **Au** Gold $4f^{14} 5d^{10} 6s^1$	80 200.59 **Hg** Mercury $4f^{14} 5d^{10} 6s^2$	81 204.38 **Tl** Thallium $4f^{14} 5d^{10} 6s^2 6p^1$	82 207.2 **Pb** Lead $4f^{14} 5d^{10} 6s^2 6p^2$	83 208.98 **Bi** Bismuth $4f^{14} 5d^{10} 6s^2 6p^3$	84 209.98 **Po** Polonium $4f^{14} 5d^{10} 6s^2 6p^4$	85 209.99 **At** Astatine $4f^{14} 5d^{10} 6s^2 6p^5$	86 222.02 **Rn** Radon $4f^{14} 5d^{10} 6s^2 6p^6$
... $d^7 7s^2$	110 269 **Ds** Darmstadtium $5f^{14} 6d^8 7s^2$	111 272 **Rg** Rontgenium $5f^{14} 6d^{10} 7s^1$	112 285 **Cn** Copernicium $5f^{14} 6d^{10} 7s^2$	113 286 **Nh** Nihonium $5f^{14} 6d^{10} 7s^2 7p^1$	114 289 **Fl** Flerovium $5f^{14} 6d^{10} 7s^2 7p^2$	115 289 **Mc** Moscovium $5f^{14} 6d^{10} 7s^2 7p^3$	116 293 **Lv** Livermorium $5f^{14} 6d^{10} 7s^2 7p^4$	117 294 **Ts** Tennessine $5f^{14} 6d^{10} 7s^2 7p^5$	118 294 **Og** Oganesson $5f^{14} 6d^{10} 7s^2 7p^6$

f-BLOCK $[(n-2)f^{1-14}(n-1)d^{0-1}ns^2]$ ← REPRESENTATIVE ELEMENTS →

INNER TRANSITION ELEMENTS

150.36 ... $f^6 6s^2$	63 151.96 **Eu** Europium $4f^7 6s^2$	64 157.25 **Gd** Gadolinium $4f^7 5d^1 6s^2$	65 158.93 **Tb** Terbium $4f^9 6s^2$	66 162.50 **Dy** Dysprosium $4f^{10} 6s^2$	67 164.93 **Ho** Holmium $4f^{11} 6s^2$	68 167.26 **Er** Erbium $4f^{12} 6s^2$	69 168.93 **Tm** Thulium $4f^{13} 6s^2$	70 173.04 **Yb** Ytterbium $4f^{14} 6s^2$	71 174.97 **Lu** Lutetium $4f^{14} 5d^1 6s^2$
244.06 ... $f^6 7s^2$	95 *243.06 **Am** Americium $5f^7 7s^2$	96 *247.07 **Cm** Curium $5f^7 6d^1 7s^2$	97 *247.07 **Bk** Berkelium $5f^9 7s^2$	98 *251.08 **Cf** Californium $5f^{10} 7s^2$	99 *252.08 **Es** Einsteinium $5f^{11} 7s^2$	100 *257.18 **Fm** Fermium $5f^{12} 7s^2$	101 *258.10 **Md** Mendelevium $5f^{13} 7s^2$	102 *259.10 **No** Nobelium $5f^{14} 7s^2$	103 *262.11 **Lr** Lawrencium $5f^{14} 6d^1 7s^2$

Atomic Masses (C^{12} = 12.00) and Electronic Configurations of Elements				
Element	**Symbol**	**Atomic Number**	**Atomic Mass**	**Electronic Configuration**
Actinium	Ac	89	227	$[Rn]^{86}\ 6d^1\ 7s^2$
Aluminium	Al	13	26.9	$[Ne]^{10}\ 3s^2\ 3p^1$
Americium	Am	95	243	$[Rn]^{86}\ 5f^7\ 7s^2$
Antimony	Sb	51	121.75	$[Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^3$
Argon	Ar	18	39.94	$[Ne]^{10}\ 3s^2\ 3p^6$
Arsenic	As	33	74.92	$[Ar]^{18}\ 3d^{10}\ 4s^2\ 4p^3$
Astatine	At	85	210	$[Xe]^{54}\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$
Barium	Ba	56	137.3	$[Xe]^{54}\ 6s^2$
Berkelium	Bk	97	247	$[Rn]^{86}\ 5f^9\ 7s^2$
Beryllium	Be	4	9.01	$[He]^2\ 2s^2$
Bismuth	Bi	83	208.98	$[Xe]^{54}\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$
Boron	B	5	10.81	$[He]^{54}\ 2s^2\ 2p^1$
Bromine	Br	35	79.90	$[Ar]^{18}\ 3d^{10}\ 4s^2\ 4p^5$
Cadmium	Cd	48	112.40	$[Kr]^{36}\ 4d^{10}\ 5s^2$
Calcium	Ca	20	40.02	$[Ar]^{18}\ 4s^2$
Californium	Cf	98	251	$[Rn]^{86}\ 5f^{10}\ 7s^2$
Carbon	C	6	12	$[He]^2\ 2s^2\ 2p^2$
Cerium	Ce	58	140.12	$[Xe]^{54}\ 4f^1\ 5d^1\ 6s^2$
Cesium	Cs	55	132.90	$[Xe]^{54}\ 6s^1$
Chlorine	Cl	17	35.45	$[Ne]^{10}\ 3s^2\ 3p^5$
Chromium	Cr	24	51.99	$[Ar]^{18}\ 3d^5\ 4s^1$
Cobalt	Co	27	58.93	$[Ar]^{18}\ 3d^7\ 4s^2$
Copernicium	Cn	112	285	$[Rn]^{86}\ 5f^{14}\ 6d^{10}\ 7s^2$
Copper	Cu	29	63.54	$[Ar]^{18}\ 3d^{10}\ 4s^1$
Curium	Cm	96	245	$[Rn]^{86}\ 5f^7\ 6d^1\ 7s^2$
Dysprosium	Dy	66	162.50	$[Xe]^{54}\ 4f^{10}\ 6s^2$
Einsteinium	Es	99	254	$[Rn]^{86}\ 5f^{11}\ 7s^2$
Erbium	Er	68	167.26	$[Xe]^{54}\ f^{12}\ 6s^2$
Europium	Eu	63	151.96	$[Xe]^{54}\ 4f^7\ 6s^2$
Fermium	Fm	100	257	$[Rn]^{86}\ 5f^{12}\ 7s^2$
Flerovium	Fl	114	289	$[Rn]^{86}5f^{14}6d^{10}7s^27p^2$
Fluorine	F	9	18.99	$[He]^2\ 2s^2\ 2p^5$
Francium	Fr	87	223	$[Rn]^{86}\ 7s^1$
Gadolinium	Gd	64	157.25	$[Xe]^{54}\ 4f^7\ 5d^1\ 6s^2$
Gallium	Ga	31	69.72	$[Ar]^{18}\ 3d^{10}\ 4s^2\ 4p^1$
Germanium	Ge	32	72.59	$[Ar]^{18}\ 3d^{10}\ 4s^2\ 4p^2$
Gold	Au	79	196.99	$[Xe]^{54}\ 4f^{14}\ 5d^{10}\ 6s^1$
Hafnium	Hf	72	178.48	$[Xe]^{54}\ 4f^{14}\ 5d^2\ 6s^2$
Hanium	Ha	105	260	$[Rn]^{86}\ 5f^{14}\ 6d^3\ 7s^2$
Helium	He	2	4	$1s^2$
Holmium	Ho	67	164.93	$[Xe]^{54}\ 4f^{11}\ 6s^2$
Hydrogen	H	1	1	$1s^1$
Indium	In	49	114.82	$[Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^1$
Iodine	I	53	126.90	$[Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^5$
Iridium	Ir	77	192.2	$[Xe]^{54}\ 4f^{14}\ 5d^7\ 6s^2$
Iron	Fe	26	55.84	$[Ar]^{18}\ 3d^6\ 4s^2$
Krypton	Kr	36	83.80	$[Ar]^{18}\ 3d^{10}\ 4s^2\ 4p^6$
Lanthanum	La	57	138.91	$[Xe]^{54}\ 5d^1\ 6s^2$
Lawrencium	Lr	103	257	$[Rn]^{86}\ 5f^{14}\ 6d^1\ 7s^2$
Lead	Pb	82	207.19	$[Xe]^{54}\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$
Lithium	Li	3	6.93	$[He]^2\ 1s^1$
Livermorium	Lv	116	293	$[Rn]^{86}\ 5f^{14}6d^{10}7s^27p^4$
Lutetium	Lu	71	174.97	$[Xe]^{54}\ 4f^{14}\ 5d^1\ 6s^2$
Magnesium	Mg	12	24.31	$[Ne]^{10}\ 3s^2$
Manganese	Mn	25	54.93	$[Ar]^{18}\ 3d^5\ 4s^2$

Element	Symbol	Atomic Number	Atomic Mass	Electronic Configuration
Mendelevium	Md	101	256	$[Rn]^{86}\ 5f^{13}\ 7s^2$
Mercury	Hg	80	200.50	$[Xe]^{54}\ 4f^{14}\ 5d^{10}\ 6s^2$
Molybdenum	Mo	42	95.94	$[Kr]^{36}\ 4d^5\ 5s^1$
Moscovium	Mc	115	289	$[Rn]^{86}\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^3$
Neodymium	Nd	60	144.24	$[Xe]^{54}\ 4f^4\ 6s^2$
Neon	Ne	10	20.18	$[He]^2\ 2s^2\ 2p^6$
Neptunium	Np	93	237	$[Rn]^{86}\ 5f^4\ 6d^1\ 7s^2$
Nickel	Ni	28	58.71	$[Ar]^{18}\ 3d^8\ 4s^2$
Nihonium	Nh	113	286	$[Rn]^{86}\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^1$
Niobium	Nb	41	92.90	$[Kr]^{36}\ 4d^4\ 5s^1$
Nitrogen	N	7	14	$[He]^2\ 2s^2\ 2p^3$
Nobelium	No	102	254	$[Rn]^{56}\ 5f^{14}\ 7s^2$
Oganesson	Og	118	294	$[Rn]^{86}\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^6$
Osmium	Os	76	190.2	$[Xe]^{54}\ 4f^{14}\ 5d^6\ 6s^2$
Oxygen	O	8	15.99	$[He]^2\ 2s^2\ 2p^4$
Palladium	Pd	46	106.4	$[Kr]^{36}\ 4d^{10}$
Phosphorus	P	15	30.97	$[Ne]^{10}\ 3s^2\ 3p^3$
Platinum	Pt	78	195.09	$[Xe]^{54}\ 4f^{14}\ 5d^9\ 6s^1$
Plutonium	Pu	94	244	$[Rn]^{86}\ 5f^6\ 7s^2$
Polonium	Po	84	210	$[Xe]^{54}\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$
Potassium	K	19	39.102	$[Ar]^{18}\ 4s^1$
Praseodymium	Pr	59	140.907	$[Xe]^{54}\ 4f^3\ 6s^2$
Promethium	Pm	61	145	$[Xe]^{54}\ 4f^5\ 6s^2$
Protactinium	Pa	91	231	$[Rn]^{86}\ 5f^2\ 6d^1\ 7s^2$
Radium	Ra	88	226	$[Rn]^{86}\ 7s^2$
Radon	Rn	86	222	$[Xe]^{54}\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$
Rhenium	Re	75	186.2	$[Xe]^{54}\ 4f^{14}\ 5d^5\ 6s^2$
Rhodium	Rh	45	102.90	$[Kr]^{36}\ 4d^8\ 5s^1$
Rubidium	Rb	37	85.47	$[Kr]^{36}\ 5s^1$
Ruthenium	Ru	44	101.07	$[Kr]^{36}\ 4d^7\ 5s^1$
Rutherfordium	Rf	104	257	$[Rn]^{86}\ 5f^{14}\ 6d^2\ 7s^2$
Samarium	Sm	62	150.35	$[Xe]^{54}\ 4f^6\ 6s^2$
Scandium	Sc	21	44.95	$[Ar]^{18}\ 3d^1\ 4s^2$
Selenium	Se	34	78.96	$[Ar]^{18}\ 3d^{10}\ 4s^2\ 4p^4$
Silicon	Si	14	28.08	$[Ne]^{10}\ 3s^2\ 3p^2$
Silver	Ag	47	107.87	$[Kr]^{22}\ 4d^{10}\ 5s^1$
Sodium	Na	11	22.98	$[Ne]^{10}\ 3s^1$
Strontium	Sr	38	87.62	$[Kr]^{36}\ 5s^2$
Sulphur	S	16	32.06	$[Ne]^{10}\ 3s^2\ 3p^4$
Tantalum	Ta	73	180.94	$[Xe]^{54}\ 4f^{14}\ 5d^3\ 6s^2$
Technetium	Tc	43	99	$[Kr]^{36}\ 4d^5\ 5s^2$
Tellurium	Te	52	127.60	$[Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^4$
Tennessine	Ts	117	294	$[Rn]^{86}\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^5$
Terbium	Tb	65	158.92	$[Xe]^{54}\ 4f^9\ 6s^2$
Thallium	Tl	81	204.37	$[Xe]^{54}\ 4f^{14}\ 5d^{10}\ 6s^2\ 6\,p^1$
Thorium	Th	90	232.03	$[Rn]^{86}\ 6d^2\ 7s^2$
Thulium	Tm	69	168.93	$[Xe]^{54}\ 4f^{13}\ 6s^2$
Tin	Sn	50	118.69	$[Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^2$
Titanium	Ti	22	47.90	$[Ar]^{18}\ 3d^2\ 4s^2$
Tungsten	W	74	183.85	$[Xe]^{54}\ 4f^{14}\ 5d^4\ 6s^2$
Uranium	U	92	238.02	$[Rn]^{86}\ 5f^2\ 6d^1\ 7s^2$
Vanadium	V	23	50.94	$[Ar]^{18}\ 3d^3\ 4s^2$
Xenon	Xe	54	131.04	$[Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^6$
Ytterbium	Yb	70	173.04	$[Xe]^{54}\ 4f^{14}\ 6s^2$
Yttrium	Y	39	88.90	$[Kr]^{36}\ 4d^1\ 5s^2$
Zinc	Zn	30	63.37	$[Ar]^{18}\ 3d^{10}\ 4s^2$
Zirconium	Zr	40	91.22	$[Kr]^{36}\ 4d^2\ 5s^2$

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Advanced level matter to explore more about the topic for competitive examinations with reference at the appropriate place in the text and detail in competition file.

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Provides definitions of new terms, laws, name reactions in organic chemistry, important facts to remember and mathematical relations.

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- AISB Qs. and State Boards' Qs. highlighted in Revision Exercises
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The second part of each chapter under the heading Competition File is planned with a target of Competitive Examinations. This provides additional useful information (not covered in the chapter). This also includes Objective Questions in the form of multiple choice type, comprehension type, matching type, matrix-match type, integer answer type and assertion reason type. Hints & Answers to almost all MCQs have been given.

PLEASE SEE THE SPECIAL FEATURES OF THE BOOK IN THE MARGINS WHICH MAKE IT NUMBER 1.

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The Study of the book will induce confidence among the students to face the challenges in the examination and achieve their target.

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SYLLABUS

CHEMISTRY

CLASS XI (THEORY)

Total Periods (Theory 160 + Practical 60)
Total Marks : 70

Time : 3 Hours | Total Marks : 70

Unit No.	Title	No. of Periods	Marks
Unit I	Some Basic Concepts of Chemistry	08	08
Unit II	Structure of Atom	10	
Unit III	Classification of Elements and Periodicity in Properties	06	04
Unit IV	Chemical Bonding and Molecular Structure	14	20
Unit V	States of Matter : Gases, Liquids and Solids	18	
Unit VI	Chemical Thermodynamics	16	
Unit VII	Equilibrium	14	
Unit VIII	Redox Reactions	06	20
Unit IX	Hydrogen	08	
Unit X	*s*-Block Elements	10	
Unit XI	*p*-Block Elements	18	
Unit XII	Organic Chemistry : Some Basic Principles and Techniques	14	18
Unit XIII	Hydrocarbons	12	
Unit XIV	Environmental Chemistry	06	
	Total	**160**	**70**

Unit I : Some Basic Concepts of Chemistry (8 Periods)

General Introduction : Importance and scope of chemistry.

Nature of matter, laws of chemical combination, Dalton's atomic theory : concept of elements, atoms and molecules.

Atomic and molecular masses, mole concept and molar mass, percentage composition, empirical and molecular formula, chemical reactions, stoichiometry and calculations based on stoichiometry.

Unit II : Structure of Atom (10 Periods)

Bohr's model and its limitations, concept of shells and subshells, dual nature of matter and light, de Broglie's relationship, Heisenberg uncertainty principle, concept of orbitals, quantum numbers, shapes of *s*, *p* and *d* orbitals, rules for filling electrons in orbitals – Aufbau principle, Pauli's exclusion principle and Hund's rule, electronic configuration of atoms, stability of half filled and completely filled orbitals.

Unit III : Classification of Elements and Periodicity in Properties (06 Periods)

Modern periodic law and the present form of periodic table, periodic trends in properties of elements – atomic radii, ionic radii, inert gas radii, ionization enthalpy, electron gain enthalpy, electronegativity, valency. Nomenclature of elements with atomic number greater than 100.

Unit IV : Chemical Bonding and Molecular Structure (14 Periods)

Valence electrons, ionic bond, covalent bond, bond parameters, Lewis structure, polar character of covalent bond, covalent character of ionic bond, valence bond theory, resonance, geometry of covalent molecules, VSEPR theory, concept of hybridization involving *s*, *p* and *d* orbitals and shapes of some simple molecules, molecular orbital theory of homonuclear diatomic molecules (qualitative idea only), hydrogen bond.

Unit V : States of Matter : Gases, Liquids and Solids (18 Periods)

Three states of matter, intermolecular interactions, types of bonding, melting and boiling points, role of gas laws in elucidating the concept of the molecule, Boyle's law, Charles law, Gay Lussac's law, Avogadro's law, ideal behaviour, empirical derivation of gas equation, Avogadro's number, ideal gas equation. Deviation from ideal behaviour, liquefaction of gases, critical temperature, kinetic energy and molecular speeds (elementary idea).

Liquid state : Vapour pressure, viscosity and surface tension (qualitative idea only, no mathematical derivations).

Solid state : Classification of solids based on different binding forces: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea). Unit cell in two dimensional and three dimensional lattices, calculation of density of unit cell, packing in solids, packing efficiency, voids, number of atoms per unit cell in a cubic unit cell, point defects, electrical and magnetic properties.

Unit VI : Chemical Thermodynamics (16 Periods)

Concepts of systems and types of systems, surroundings, work, heat, energy, extensive and intensive properties, state functions. First law of thermodynamics – internal energy and enthalpy, heat capacity and specific heat, measurement of ΔU and ΔH, Hess's law of constant heat summation, enthalpy of bond dissociation, combustion, formation, atomization, sublimation, phase transition, ionization, solution and dilution. Second law of thermodynamics (brief introduction).

Introduction of entropy as a state function, Gibb's energy change for spontaneous and non-spontaneous processes, criteria for equilibrium. Third law of thermodynamics (brief introduction).

Unit VII: Equilibrium (14 Periods)

Equilibrium in physical and chemical processes, dynamic nature of equilibrium, law of mass action, equilibrium constant, factors affecting equilibrium – Le Chatelier's principle; ionic equilibrium – ionization of acids and bases, strong and weak electrolytes, degree of ionization, ionization of polybasic acids, acid strength, concept of pH. Henderson equation, hydrolysis of salts (elementary idea), buffer solutions, solubility product, common ion effect (with illustrative examples).

Unit VIII : Redox Reactions (06 Periods)

Concept of oxidation and reduction, redox reactions, oxidation number, balancing redox reactions in terms of loss and gain of electrons and change in oxidation number, applications of redox reactions.

Unit IX : Hydrogen (08 Periods)

Position of hydrogen in periodic table, occurrence, isotopes, preparation, properties and uses of hydrogen, hydrides-ionic, covalent and interstitial; physical and chemical properties of water, heavy water, hydrogen peroxide-preparation, reactions and structure and use; hydrogen as a fuel.

Unit X : s-Block Elements (Alkali and Alkaline Earth Metals) (10 Periods)

Group 1 and Group 2 elements :

General introduction, electronic configuration, occurrence, anomalous properties of the first element of each group, diagonal relationship, trends in the variation of properties (such as ionization enthalpy, atomic and ionic radii), trends in chemical reactivity with oxygen, water, hydrogen and halogens, uses.

Preparation and properties of some important compounds : Sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogen carbonate, biological importance of sodium and potassium.

Calcium oxide and calcium carbonate and their industrial uses, biological importance of magnesium and calcium.

Unit XI : *p*-Block Elements (18 Periods)

General Introduction to *p*-Block Elements

Group 13 Elements : General introduction, electronic configuration, occurrence, variation of properties, oxidation states, trends in chemical reactivity, anomalous properties of first element of the group, Boron – physical and chemical properties, some important compounds, borax, boric acids, boron hydrides, Aluminium : Reactions with acids and alkalies, uses.

Group 14 Elements : General introduction, electronic configuration, occurrence, variation of properties, oxidation states, trends in chemical reactivity, anomalous behaviour of first elements. Carbon-catenation, allotropic forms, physical and chemical properties; uses of some important compounds: oxides. Important compounds of silicon and a few uses: Silicon tetrachloride, silicones, silicates and zeolites their uses.

Group 15 Elements : General introduction, electronic configuration, occurrence, oxidation states, trends in physical and chemical properties; Nitrogen-preparation, properties and uses; compounds of nitrogen, preparation and properties of ammonia and nitric acid, oxides of nitrogen (structure only); phosphorus-allotropic forms, compounds of phosphorus: Preparation and properties of phosphine, halides and oxoacids (elementary idea only).

Unit XII : Organic Chemistry – Some Basic Principles and Techniques (14 Periods)

General introduction, methods of purification, qualitative and quantitative analysis, classification and IUPAC nomenclature of organic compounds. Electronic displacements in a covalent bond : inductive effect, electromeric effect, resonance and hyper-conjugation. Homolytic and heterolytic fission of a covalent bond : free radicals, carbocations, carbanions, electrophiles and nucleophiles, types of organic reactions.

Unit XIII : Hydrocarbons (12 Periods)

Classification of Hydrocarbons

Aliphatic Hydrocarbons:

Alkanes – Nomenclature, isomerism, conformation (ethane only), physical properties, chemical reactions including free radical mechanism of halogenation, combustion and pyrolysis.

Alkenes – Nomenclature, structure of double bond (ethene), geometrical isomerism, physical properties, methods of preparation, chemical reactions : addition of hydrogen, halogen, water, hydrogen halides (Markownikov's addition and peroxide effect), ozonolysis, oxidation, mechanism of electrophilic addition.

Alkynes – Nomenclature, structure of triple bond (ethyne), physical properties, methods of preparation, chemical reactions : acidic character of alkynes, addition reaction of hydrogen, halogens, hydrogen halides and water.

Aromatic hydrocarbons – Introduction, IUPAC nomenclature, benzene : resonance, aromaticity, chemical properties, mechanism of electrophilic substitution. Nitration, sulphonation, halogenation, Friedel Craft's alkylation and acylation, directive influence of a functional group in mono-substituted benzene. Carcinogenicity and toxicity.

Unit XIV : Environmental Chemistry (06 Periods)

Environmental pollution – air, water and soil pollution, chemical reactions in atmosphere, smog, major atmospheric pollutants, acid rain, ozone and its reactions, effects of depletion of ozone layer, greenhouse effect and global warming – pollution due to industrial wastes, green chemistry as an alternative tool for reducing pollution, strategies for control of environmental pollution.

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SOME BASIC CONCEPTS OF CHEMISTRY

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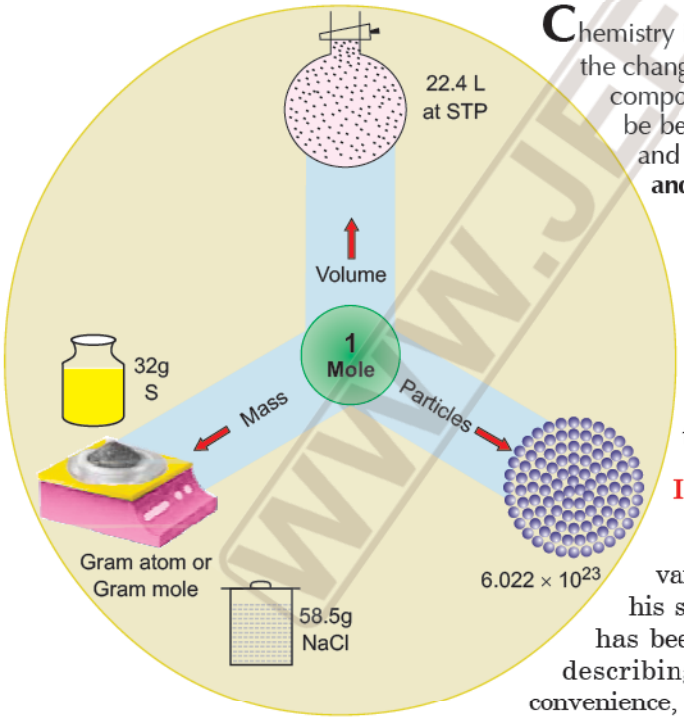

Chemistry is the study of the materials that make up the universe and the changes which these materials undergo. The study deals with the composition, structure and properties of matter. These aspects can be best understood in terms of the constituents of matter: **atoms** and **molecules.** In fact, chemistry is called the **science of atoms and molecules**.

Can we see, weigh and perceive the atoms and molecules ?

Can we count the number of atoms and molecules in a given mass of matter ?

These are some curious questions which come to our mind. In the present unit, we will learn the answers of some of these questions.

IMPORTANCE OF CHEMISTRY

The material world around us consists of an enormous variety of substances. Man has been curious to know about his surroundings ever since he came into existence. Science has been helping the man to systematize his knowledge for describing and understanding the nature. For the sake of convenience, science is subdivided into various disciplines. The main disciplines of science are : chemistry, physics, biology, geology, etc.

Chemistry *is the branch of science which deals with the study of composition, properties and structures of matter and the changes which the matter undergoes under different conditions and the laws which govern these changes.*

Chemistry plays a central role in science and is often interlinked with other branches of science. It also plays an important role in our daily life.

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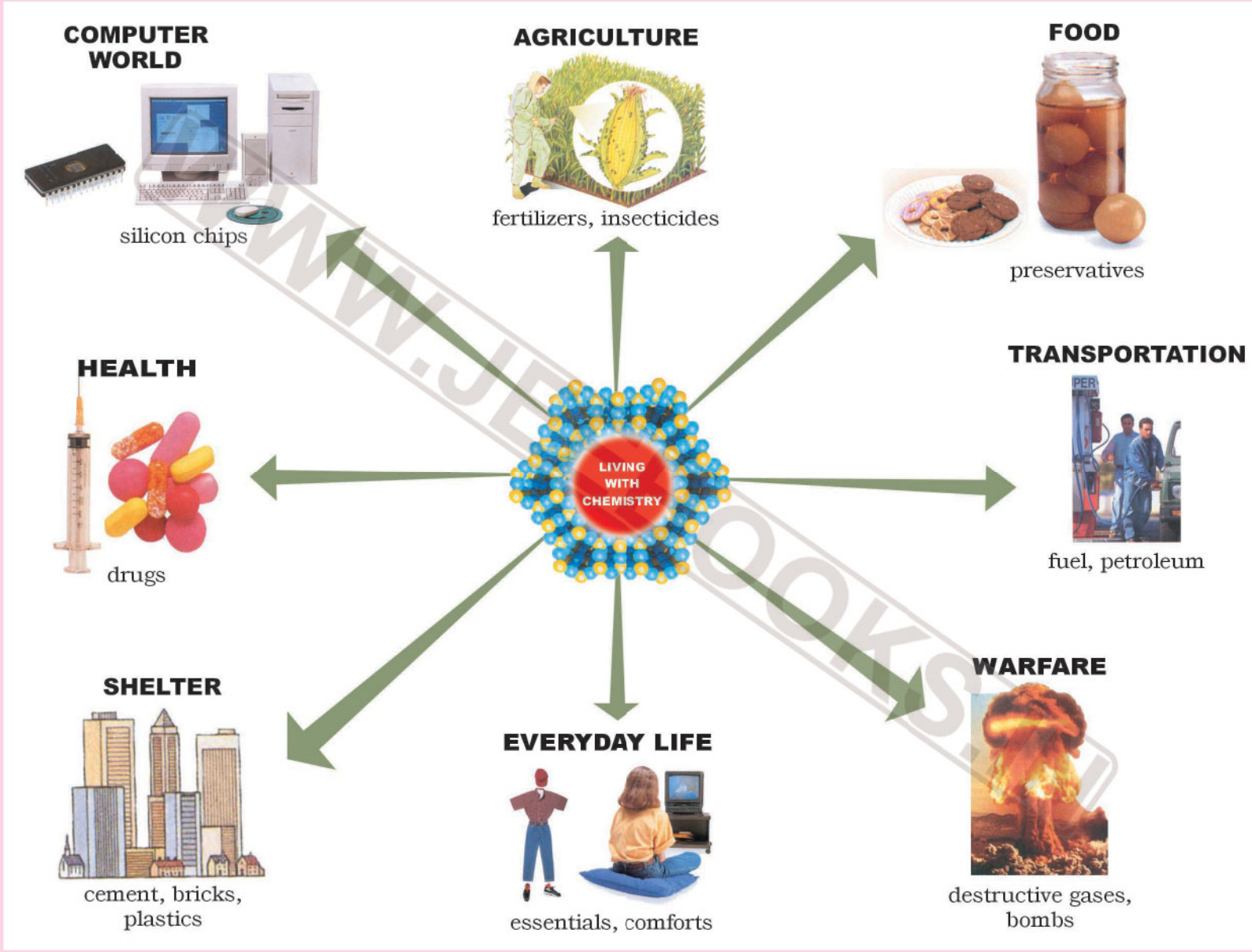

Fig. 1 Applications of chemistry in different fields.

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Scope of Chemistry

In chemistry, we study the composition of materials to find out what they are made of. The marvellous thing about chemistry is that all the matter in the universe is made up of tiny smallest particles called **atoms** or **molecules.** It is very interesting that only about 118 types of atoms make up whole of the matter in the universe. We also learn how their composition affects their characteristics and behaviour so that we can plan to make new materials with properties of our interests. For this, we have to learn how substances undergo changes in composition and properties. These changes in the language of chemistry are called **chemical reactions.** Thus, studying chemistry is essential for us to understand better the world in which we live.

Since there is a large variety of substances in the universe, the scope of chemistry is immense. Whether we are concerned with living systems in biology and medicine, with materials such as iron, steel and concrete as in engineering or with manufacture of computer chips, we deal with chemistry. Progress in modern society is completely based on advances in chemistry. In today's technological age, the importance of chemistry is increasing. Chemical principles are playing key role in diverse areas such as weather patterns, functioning of brain and operation of computers.

It is difficult today to imagine our life without chemistry.

Main Applications of Chemistry

Chemistry has helped in agriculture, food, medicine, warfare, transportation, computers and in our everyday life. The important applications of chemistry in different fields are shown in Fig. 1. and are discussed below:

Chemistry for meeting our basic needs and necessities of life.

Chemistry has helped significantly in meeting human needs for food, health care products and other necessities of life.

- Chemistry has provided ***chemical fertilizers,*** improved varieties of ***insecticides, fungicides*** and ***pesticides*** to increase the yield of crops and fruits.
- The use of ***preservatives*** has helped to keep food materials for longer periods.
- Chemistry has also helped for **better health and sanitation**. The epidemics such as cholera, small pox, plague have now become things of the past.
- The discovery of **anaesthetics** has made surgical operations more and more successful.
- Chemistry has also given us a variety of drugs such as **antipyretics** (to lower body temperature in high fever), **analgesics** (to relieve pain), **tranquilizers** (for treatment of stress and mental diseases), **antimicrobials** (to cure infections), **antimalarials** (to treat malaria) etc. **Antibiotics** such as penicillin, amoxycillin, streptomycin and ***broad spectrum antibiotics*** such as tetracycline, chloramphenicol, etc. have cured a variety of diseases due to harmful micro-organisms. ***Antifertility drugs*** have been world-wide used for birth control methods.

Chemistry has given us a large number of **life *saving drugs***.

> Life saving drugs like ***cisplatin*** and ***taxol*** for cancer therapy and **AZT** (azidothymidine) used for helping AIDS victims are latest contributions of chemistry in medicines.

Chemistry for our comforts, pleasure and luxuries

Chemistry has also pioneer contribution towards our comforts, pleasure and luxuries.

- It has given us building materials, synthetic fibres and variety of articles of domestic use.
- Chemical industries manufacturing fertilizers, acids, alkalies, salts, dyes, polymers, drugs, soaps, detergents, metals, alloys and other organic and inorganic chemicals including new materials have improved our national economy.

Chemistry for giving us new materials

In recent years, chemistry has given us new materials such as super-conducting ceramics, conducting polymers, optical fibres, microalloys, carbon fibres, etc.

Chemistry in war

Chemistry has also increased the striking power of a country in war times. It is responsible for the discovery of highly explosive substances such as dynamite, TNT (trinitrotoluene), nitroglycerine, poisonous gases such as mustard gas, phosgene, lewisite and many deadly weapons such as atom bomb and hydrogen bomb.

Future Goals and Challenges for Chemistry

In recent years, chemistry has solved with a fair degree of success some of the challenging aspects of environmental degradation. So far alternatives to environmentally hazardous refrigerants like CFCs (chlorofluoro carbons), responsible for ozone depletion in the stratosphere has been successfully developed. Still many goals are there for the chemists to achieve successfully. Environmental problems, management of Green house gases (like methane, carbon dioxide, etc.) understanding bio-chemical processes, use of enzymes for large scale production of chemicals, synthesis of exotic materials are some main challenges for the future chemists. A developing country like India looks forward towards intelligent, talented and creative chemists for accepting these challenges.

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NATURE OF MATTER

The entire universe is made up of matter and energy.

Anything that has mass and occupies space is called **matter.**

The presence of matter can be felt by one or more of our senses. Everything around us, for example, book, pen, table, sugar cubes, iron rod, water, air are composed of matter because they have mass and they occupy space.

Matter can be **classified** in two ways :

A : *Physical classification of matter*

B : *Chemical classification of matter.*

A : Physical Classification of Matter

Depending upon the physical state of matter, it can be classified into three states, namely, *solid, liquid* and *gaseous state.*

(*i*) Solid state. *A solid has a definite shape and definite volume.* Thus, solids are generally hard and rigid. For example, wood, table, copper rod, common salt, etc.

(*ii*) Liquid state. *A liquid has a definite volume but not definite shape.* A liquid takes the shape of the container in which it is placed. For example, water, milk, oil, etc.

(*iii*) Gaseous state. *A gas neither possesses a definite volume nor a definite shape.* It occupies the whole of the volume of the vessel in which it is placed. For example, air, oxygen, hydrogen, carbon dioxide, etc.

Particle Nature of Matter

As we know matter is made up of particles. In terms of particle concept of matter, in **solids**, the particles are closely packed and the empty spaces between the particles are very small. Due to close packing of the particles, they can only vibrate about their fixed positions i.e. *can have only vibratory motion.* Due to fixed positions of the particles in solids, they have highly ordered arrangement and this gives definite regular shape to the crystals. The regular ordered arrangement of particles in solids is called **lattice.**

The attractive forces among the particles called interparticle forces are strong in solids. Thus, **solids have a definite shape and a definite volume.**

In **liquids**, the particles are loosely packed and empty spaces between them are relatively large. Due to loose packing, the attractive forces between them are relatively weak. However, these are not weak enough to allow the particles to separate from one another. Thus, **liquids have definite volume but donot have fixed shape.** They take the shape of the container.

On the other hand, in **gases**, the particles are very loosely packed and empty spaces between them are very large. As a result, the attractive forces between the particles are very very small so that their movement is easy and fast. They can move to each corner of the vessel and therefore **gases donot have definite shape and definite volume.**

Because of such arrangement of particles, different states of matter exhibit different characteristics. The arrangement of particles in solids, liquids and gaseous state is shown in Fig. 2.

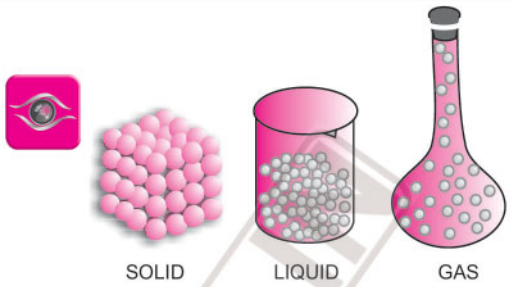

Fig. 2. Arrangement of particles in solid, liquid and gaseous state.

These three states of matter are interconvertible by changing the conditions of temperature and pressure. On heating, a solid changes to a liquid and on further heating the liquid changes to the gaseous (or vapour) state. In the reverse process, a gas on cooling liquefies to the liquid and liquid on further cooling freezes to the solid.

$$\text{SOLID} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{LIQUID} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{GAS}$$

B. Chemical Classification of Matter

The chemical classification of matter is based upon its composition. Different substances differ from each other in their constituents composition. On the basis of chemical composition, matter can be classified as :

A : Pure substances

B : Mixtures

A. Pure substances

Pure substances *consist of single type of particles.* All the constituent particles of a pure substance are same in their chemical nature. For example, copper, silver, gold, water, glucose, sodium chloride (common salt) are some examples of pure substances. As we know, water contains hydrogen and oxygen but they are always present in a fixed ratio and therefore, like all other pure substances behave as single substance having fixed chemical composition. Similarly, glucose contains carbon, hydrogen and oxygen in a fixed ratio and thus behaves as a pure substance. The constituents of pure substances cannot be separated by simple physical methods (like filtration, evaporation, distillation, sublimation, mechanical separation, etc.). These can only be separated by chemical or electrochemical methods.

Pure substances can be further classified into **elements** and **compounds**.

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1. Element

An element is the simplest form of a pure substance. It may be defined as :

the simplest form of a pure substance which can neither be decomposed into nor built from simpler substances by ordinary physical or chemical methods.

The common examples of elements are hydrogen, oxygen, nitrogen, sulphur, iron, lead, gold, mercury, etc. There are about 118 elements known at present. Out of these, 92 have so far been found to occur naturally and the remaining have been prepared in the laboratory. All the elements do not occur in the crust of earth in equal proportions. About twenty elements make up 99% of the earth's crust. The most abundant elements in the earth's crust are oxygen, silicon, aluminium, iron, calcium, sodium, potassium, hydrogen, chlorine, carbon, etc.

Elements are further classified into following types :

(*a*) Metals. These elements are generally solids and possess characteristics such as *bright lustre, hardness and ability to conduct electricity and heat.* These are generally malleable (can be beaten into thin sheets) and ductile (can be drawn into wires). Some common examples of metals are copper, iron, silver, gold, aluminium, etc. About 80% of the known elements are metals.

(*b*) Non-metals. These elements are generally *non lustrous, brittle and poor conductors of heat and electricity.* The common examples of non-metals are carbon, hydrogen, oxygen, nitrogen, etc.

(*c*) Metalloids. *These are elements which have characteristics common to both metals and non-metals.* The common examples of metalloids are silicon, arsenic, bismuth, antimony, etc.

2. Compound

Compounds are pure substances containing more than one kind of element. A compound may be defined as :

a pure substance containing two or more than two elements combined together in a definite proportion by mass and which can be decomposed into its constituent elements by suitable chemical methods.

A compound always contains the same elements in *definite* or *fixed proportion* by weight. For example, water always contains hydrogen and oxygen in the ratio of 1 : 8 by mass.

Similarly, carbon dioxide always contains carbon and oxygen in the ratio of 3 : 8.

The properties of the compounds are totally different from the elements from which these are formed. For example, *hydrogen is combustible while oxygen is supporter of combustion but water (a compound of hydrogen and oxygen) is normally used for extinguishing fire.*

The compounds may be classified into two types as :

(*a*) Inorganic compounds. These are the compounds which are obtained from non-living sources such as rocks, minerals, etc. For example, common salt, marble, washing soda, etc.

(*b*) Organic compounds. These are the compounds which are obtained from living sources such as plants and animals. All these contain carbon. For example, carbohydrates, oils, fats, waxes, proteins, etc.

B. Mixtures

Mixtures contain more than one kind of pure form of matter, known as **substance.** It is a simple combination of two or more substances in which the constituent substances retain their identities. The composition of the mixture may be varied to any extent. The substances present in a mixture are called its **components**. Therefore, a mixture may contain two or more substances in any ratio. Thus, a mixture may be defined as :

a combination of two or more elements or compounds in any proportion so that the components do not lose their identity.

Many of the substances present around us are mixtures. For example, sugar solution in water, air, tea, brass (an alloy of copper and zinc), soft drink, soil, etc are all mixtures.

Mixtures are of two types :

(*a*) *Homogeneous mixture*
(*b*) *Heterogeneous mixture*

(*a*) Homogeneous mixture. *A mixture is said to be homogeneous if it has a uniform composition throughout.* The components of a mixture cannot be seen even under a powerful microscope. Homogeneous mixtures are also called **solutions.** Some examples of homogeneous mixtures are air, gasoline, sea water, brass, etc. Air is a homogeneous mixture of a number of gases such as oxygen, nitrogen, carbon dioxide, water vapour, etc. The composition of air is the same everywhere.

(*b*) Heterogeneous mixture. *A mixture is said to be heterogeneous if its composition is not uniform throughout.* These mixtures consist of two or more parts (called phases) which have different compositions. These have visible boundaries of separation between the different constituents and can be easily seen even with naked eye. For example, a mixture of iron filings, common salt and sulphur gives a heterogeneous mixture in which the components can be seen lying side by side very easily.

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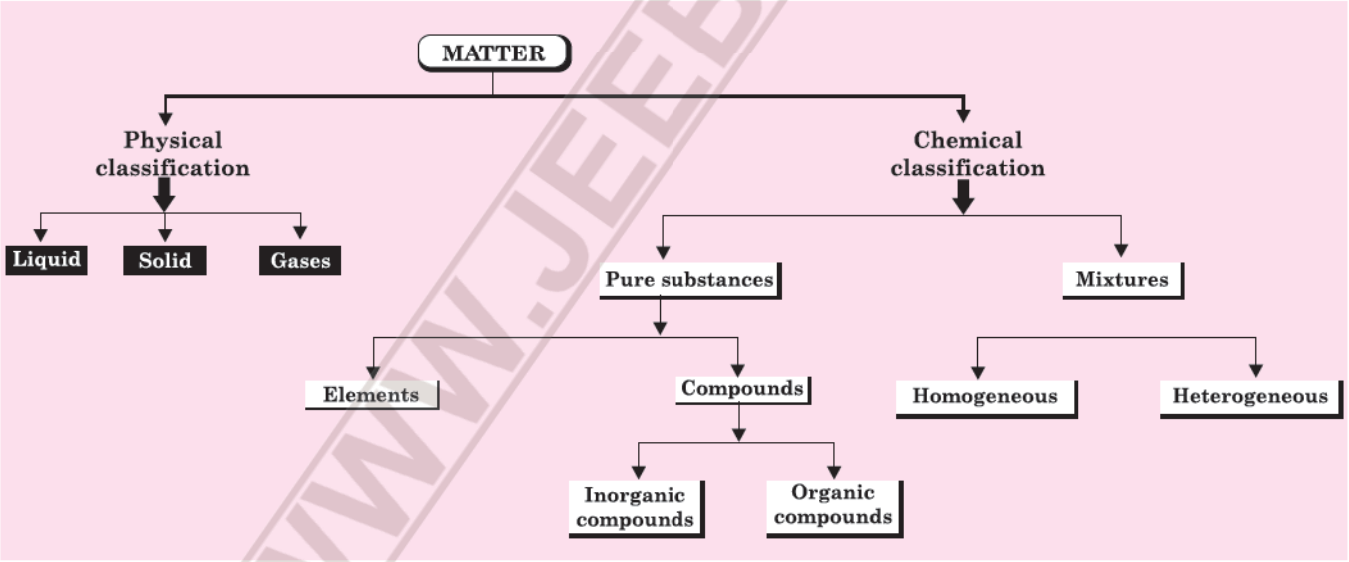
Differences between Compound and Mixture

Let us sum up important differences between compounds and mixtures.

Compounds	Mixtures
1. In a compound, two are more elements are combined chemically.	1. In a mixture, two or more elements or compounds just mix together.
2. The compounds contains two or more elements in a fixed ratio by mass. Its composition is always fixed.	2. The components of a mixture may be present in any ratio. Its composition is variable.
3. A compound has a definite formula.	3. A mixture does not have a definite formula.
4. A compound is always homogeneous i.e., has the same composition throughout.	4. A mixture may be homogeneous or heterogeneous.
5. A chemical reaction takes place and therefore, the formation of a compound takes place with absorption or evolution of energy.	5. No chemical reaction takes place and therefore, the formation of mixture is not accompained by any energy change.
6. The properties of a compound are entirely different from those of its constituents.	6. A mixture shows the properties of its constituents.
7. A compound cannot be separated into its constituents by ordinary physical methods. These can be separated by chemical or electrochemical reactions.	7. A mixture can be separated into its constituents by physical methods (like filtration, evaporation, distillation, sublimation, mechanical separation etc.)
8. A compound has a fixed melting point, boilling point, etc.	8. A mixture does not have fixed melting point, boiling point, etc.

The classification of matter has been summed up below :



PROPERTIES OF MATTER AND THEIR MEASUREMENT

Every substance has unique or characteristic properties. These properties may be classified as **physical properties** and **chemical properties**.

> **Physical properties** are those **properties which can be measured or observed without changing the identity or composition of the substance**.

For example, colour, odour, melting point, boiling point, density, etc. On the other hand,

> **chemical properties are those properties in which a chemical change in the substance takes place**.

The observation or measurement of chemical properties involve chemical reactions. The examples of chemical properties are characteristic reactions of different substances such as acidity, basicity, combustibility and reactions with other elements and compounds.

Many physical properties of matter such as mass, length, volume, temperature, pressure, density, etc. are quantitative in nature. Therefore, these properties are also called physical quantities.

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Expressing a Physical Quantity

The value of a physical quantity is always expressed in two parts :

(*i*) *numerical value* and (*ii*) *unit.*

For example, we may express correctly the weight of a box as 5700 g or 5.7 kg. The simple numerical figure 5700 or 5.7 does not convey any meaningful information. Thus, it is essential to include units with every experimental value. A **unit** is defined as

the standard of reference chosen to measure any physical quantity.

Naturally, we must have a convenient system of units for assigning numerical values to the measured or calculated values. Fortunately, it turns out that it is sufficient to define **some basic units** such as units of **mass**, **length** and **time**. Since *these are independent units and cannot be derived from any other unit,* these are also called **fundamental units**.

The units for other quantities can be derived from these units and hence are called **derived units.**

There are many different systems of units. For the first time in 1791, a study committee of the **French Academy of Science** devised a system called *"the metric system"* which became popular in the scientific community throughout the world. The fundamental units of metric system are the **grams** for *mass,* the **metre** for *length* and the **litre** for the *volume***.** In India, the metric system was adopted in 1957. The metric system is a decimal system and the different units for a physical quantity are related in powers of ten. The different powers are generally indicated by a prefix attached to the unit.

SI Units

In recent years, the scientists have generally agreed to use the **International System of Units** abbreviated as SI units. These units were adopted by *General Conference of Weights and Measures in 1960.* These are abbreviated as **SI** and the designation comes from its French name **Systeme Internationale**.

The SI system has ***seven base units*** and are listed in Table 1. These base units pertain to seven fundamental scientific quantities and all other units can be derived from these.

Table. 1. Seven Base SI Units.

Physical Quantity	Symbol for quantity	Name of Unit	Symbol
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Thermodynamic temperature	T	kelvin	K
Electric current	I	ampere	A
Luminous intensity	I_v	candela	cd
Amount of substance	n	mole	mol

It may be noted that the unit of temperature according to SI system is Kelvin but still celsius scale (°C) of temperature is commonly used in our daily life. These two units are related as :

Kelvin temperature (K) = °C + 273.15

Similarly, **Angstrom** (Å) is commonly used as a unit of length in chemistry. It is almost of the same size as the size of an atom. It is equal to 10^{-10} m.

$$\mathbf{1\ \text{Å} = 10^{-10}\ m}$$

However, it must be kept in mind that it is not SI unit. In SI units, we may use *nanometre (nm)* or *picometre (pm) :*

$$\mathbf{1\ nm = 10^{-9}\ m}$$

$$\mathbf{1\ pm = 10^{-12}\ m}$$

The definitions of the SI base units are given in Table 2.

Table 2. Definitions of seven SI base units.

Measured Quantity	Unit	Definition
Length	**metre**	The ***metre*** is the length of the path travelled by light in vacuum during a time interval of 1/299, 792,458 of a second.
Mass	**kilogram**	The ***kilogram*** is the unit of mass and is equal to the mass of the international prototype of the kilogram. It is also defined as the mass of a platinum block stored at the International Bureau of Weights and Measures in France.
Time	**second**	The ***second*** is the duration of 9, 192, 631, 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium- 133 atom.
Electric current	**ampere**	The ***ampere*** is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible cross-section, and placed one metre apart in vacuum, would produce between these conductors a force equal to 2×10^{-7} newton per metre of length.
Thermodynamic temperature	**kelvin**	The ***kelvin*** is the unit of thermodynamic temperature and equals exactly 1/273.16 of the thermodynamic temperature of the triple point of water.
Amount of substance	**mole**	The ***mole*** is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon–12.
Luminous intensity or Luminosity	**candela**	The ***candela*** is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

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PREFIXES

The SI units of some of the physical quantities are either too small or too large. To change the order of magnitude, these are expressed by using *prefixes* before the name of the base units. The various perfixes are listed in Table 3.

Table 3. List of common prefixes used in SI system.

Multiple	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-1}	deci	d	10^{1}	deka	da
10^{-2}	centi	c	10^{2}	hecto	h
10^{-3}	milli	m	10^{3}	kilo	k
10^{-6}	micro	μ	10^{6}	mega	M
10^{-9}	nano	n	10^{9}	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f	10^{15}	peta	P
10^{-18}	atto	a	10^{18}	exa	E
10^{-21}	zepto	z	10^{21}	zetta	Z
10^{-24}	yocto	y	10^{24}	yotta	Y

SOME COMMONLY USED QUANTITIES

Let us learn about some common quantities which we often come across.

1. Mass and weight.

Mass of a substance *is the amount of matter present in it.*

Weight is *the force exerted on an object by the pull of gravity.* The mass of a substance is constant and is independent of its location. For example, your body has same mass whether you are on Earth or on the moon. However, *weight of an object may change from one place to another due to change in gravity*. The mass of a substance can be measured very accurately in the laboratory by using an analytical balance. An analytical balance commonly used in laboratories is shown in Fig. 3 (*a*). These days, many types of electronic balances are available (Fig. 3 *b*). The analytical balances usually weigh to ± 0.0001 g, although some balances are available which can weigh to ± 0.00001 g.

The SI unit of mass is **kilogram**, (kg). Because kilogram is too large unit for many purposes, its fraction, gram, g, is commonly used and 1 kg = 1000 g. The smaller units such as milligram, mg (1mg = 10^{-3} g), microgram, μg (1 μg = 10^{-3} mg or = 10^{-6} g) are also commonly used.

$$1\ kg = 10^3\ g = 10^6\ mg = 10^9\ \mu g$$
$$1g = 10^3\ mg = 10^6\ \mu g$$
$$1\ mg = 10^3\ \mu g$$

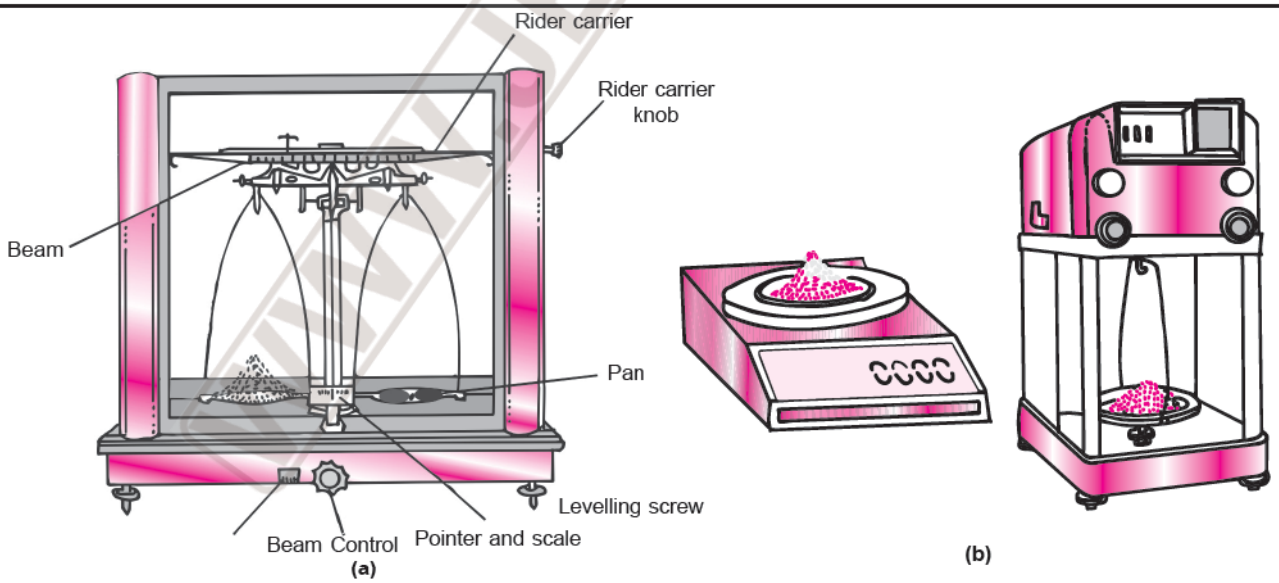

Fig. 3. (a) Analytical balance (b) Electronic balances.

2. Volume

Volume is the *amount of space occupied by an object.* It has the units of (length)^3. So in SI system, volume has units cubic metre, m^3 and is defined as ***the amount of space occupied by a cube having each edge of 1 metre.*** But in laboratories smaller volumes are commonly used. Hence, smaller units such as cubic decimetre, dm^3 ($1dm^3 = 10^{-3}\ m^3$) and cubic centimetre, cm^3 ($1cm^3 = 0.001\ dm^3$ or $= 10^{-6} m^3$) are commonly used.

However, it may be noted that in normal use, volume of liquids are commonly expressed in more familiar units

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such as litre, L and millilitre, mL. Litre is equal in size to dm^3 and millilitre is equal in size to cm^3.

$$1L = 1dm^3 \text{ and } 1mL = 1\ cm^3$$
$$\text{and } 1L = 1000\ mL = 1000\ cm^3 = 1dm^3$$

These relationships can be understood from Fig. 4.

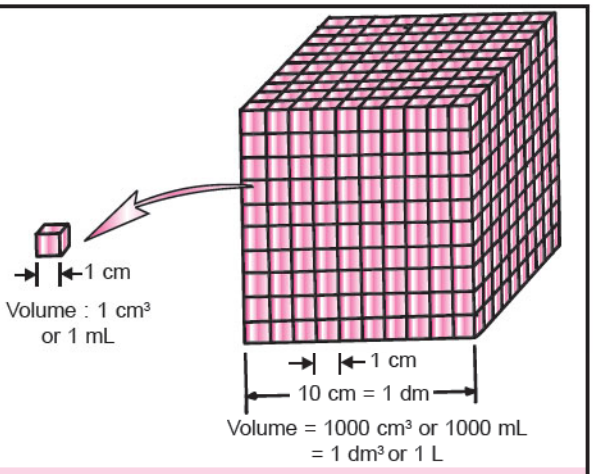

Fig. 4. Comparison between the relative sizes of two units of volume.

The volume of liquids or solutions are commonly measured in the laboratory by *graduated cylinder*, *burette* or *pipette*. A volumetric flask is used to prepare a known volume of a solution. Volumetric flasks of different volumes are available. These devices for measuring volume are shown in Fig. 5. A precise volume of a liquid can also be measured with the help of *graduated syringe*.

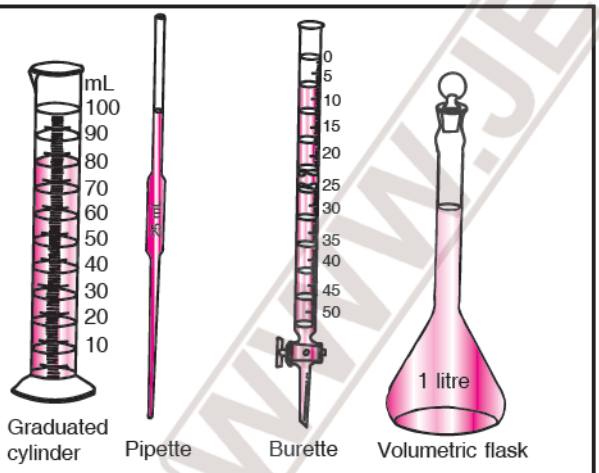

Fig. 5. Some volume measuring devices.

3. Measuring Density

Density of a substance is ***its amount of mass per unit volume***. So, density is the property which relates the mass of an object to its volume. It is simply the ***mass of an object divided by its volume.*** The units of density may be obtained as :

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{SI unit of density} = \frac{\text{SI unit of mass}}{\text{SI unit of volume}}$$

$$= \frac{\text{kg}}{\text{m}^3} \text{ or kg m}^{-3}$$

This unit is quite large and it is commonly expressed as g cm^{-3} for solids and g mL^{-1} for liquids, where mass is expressed in gram and volume in cm^3 or mL. As we know that volume of a substance changes when heated or cooled, therefore, densities depend upon temperature. Hence, *while reporting a density, the temperature must also be mentioned.*

4. Temperature

Temperature *measures the degree of hotness or coldness of an object.* There are three common scales to measure temperature

1. **The SI scale or Kelvin scale measured in Kelvin (K)**
2. **Celsius scale measured in degree Celsius (°C)**
3. **Fahrenheit scale measured in degrees Fahrenheit (°F)**

The Fahrenheit scale has been commonly used in United States and is slowly been replaced by Celsius scale and Kelvin scale. The thermometers with celsius scale are calibrated from 0° to 100° where these two temperatures are the freezing point and boiling point of water respectively.

The Fahrenheit scale is represented between 32° to 212° which represent freezing point and boiling point of water respectively. There are 100 degrees between these two points on the celsius scale but 180° degrees between them in Fahrenheit giving rise to exact relationship as

$$180°\ F = 100°C \quad \text{or } 1.8°F = 1°C$$

The temperatures on two scales are related to each other by the following relationship :

$$°F = \frac{9}{5}(°C) + 32°$$

So to convert **Celsius to Fahrenheit**, we can use the formula

$$°F = \frac{9}{5}(°C) + 32°$$

and to convert **Fahrenheit to Celsius**, we can use the formula,

$$°C = \frac{5}{9}[°F - 32°]$$

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According to SI system, the unit of temperature is **Kelvin.** One kelvin is the same size as one degree celsius. On Kelvin scale, the lowest possible temperature is equal to 0 Kelvin or 0 K. It may be noted that **kelvin temperature is written without a degree sign.** On this scale, the freezing point of water is – 273.15 K and boiling point of water is 373.15 K. The coldest possible temperature 0 K becomes –273.15°C and it is also sometimes called **absolute zero.**

The Kelvin scale is related to Celsius scale as :

$$K = °C + 273.15$$

or $K = °C + 273$ (for simplicity)

so that

Temperature in Kelvin = Temperature in °C + 273.15
Temperature in °C = Temperature in K – 273.15

For example, the human body temperature and room temperature on these temperature scales are :
Human body temperature = 98.6°F = 37°C = 310.15 K
Room temperature = 77°F = 25°C = 298.15K

The three types of thermometers using different scales are shown in Fig. 6.

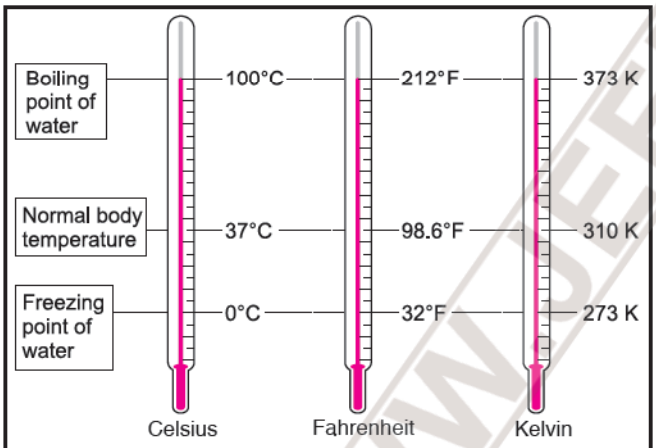

Fig. 6. Thermometers using different temperature scales.

It is interesting to note that temperature below 0°C (*i.e.* –ve values) are possible in Celsius scale but in Kelvin scale, negative values of temperature are not possible.

DERIVED UNITS

The units of different physical quantities can be derived from the seven base units. These are called **derived units** because these are derived from the base units. For deriving these units, we can multiply or divide the symbols for units as if they are algebraic quantities. For example, to determine the volume of a box, we multiply length, breadth and height as :

Volume = Length × Breadth × Height

If units of length are m,

Volume = $m \times m \times m = m^3$

Therefore, **the SI units of volume are m^3.** If length, breadth and height of the box are 1.0 m, 2.0 m and 3.0 m respectively, then volume in terms of SI units may be expressed as :

Volume = (1.0 m) × (2.0 m) × (3.0 m) = 6.0 m^3

The other units may also be built up in this way from the definition of the physical quantity. For example,

(*i*) **Area**. The units of area can be easily derived as :

$$\text{Area} = \text{Length} \times \text{Breadth}$$
$$= m \times m = m^2$$

(Units of length are m)

(*ii*) **Density.** The density of a substance is mass per unit volume, *i.e.*

$$\text{Density} = \frac{\text{Mass of sample}}{\text{Volume of sample}} = \frac{\text{kg}}{\text{m}^3}$$
$$= \mathbf{kg\ m^{-3}}$$

(*iii*) **Velocity.** It is the change in distance per unit time, *i.e.*

$$\text{Velocity} = \frac{\text{Distance}}{\text{Time}} = \frac{\text{m}}{\text{s}}$$
$$= \mathbf{m\ s^{-1}}$$

(*iv*) **Acceleration.** It is change in velocity per unit time, *i.e.*

$$\text{Acceleration} = \frac{\text{Velocity}}{\text{Time}}$$
$$= \frac{(\text{m s}^{-1})}{(\text{s})}$$
$$= \mathbf{m\ s^{-2}}$$

(*v*) **Force.** It is mass multiplied by acceleration.

$$\text{Force} = \text{Mass} \times \text{Acceleration}$$
$$= (\text{kg}) \times (\text{m s}^{-2})$$
$$= \mathbf{kg\ m\ s^{-2}}$$

(*vi*) **Pressure.** Pressure is force per unit area, *i.e.*

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

But force has the derived units as kg m s^{-2}.

$$\therefore \quad \text{Units of pressure} = \frac{\text{kg m s}^{-2}}{\text{m}^2}$$
$$= \mathbf{kg\ m^{-1}\ s^{-2}}$$

Some common **derived units** are given in Table 4.

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Table 4. Some common SI derived units.

Physical quantity	Relation with other basic quantities	Unit	Symbol and definition
Area	Length square	—	m^2
Volume	Length cube	—	m^3
Density	Mass per unit volume	—	Kg/m^3 or $kg\ m^{-3}$
Speed	Distance travelled per unit time	—	m/s or $m\ s^{-1}$
Acceleration	Speed change per unit time	—	m/s × 1/s or $m\ s^{-2}$
Force	Mass × acceleration	Newton*	$N = kg\ m\ s^{-2}$
Pressure	Force per unit area	Pascal	$Pa = kg\ m^{-1}\ s^{-2}$
Energy, work	Force × distance travelled	Joule**	$J = kg\ m\ s^{-2} \times m$ or $kg\ m^2\ s^{-2}$
Power	Energy/Time	Watt	$W = kg\ m^2\ s^{-3}$ or Js^{-1}
Electric charge or potential difference	Current × time	Coulomb	C = As
Electric resistance	Potential difference/current	Ohm	$\Omega = VA^{-1}$
Electrical conductance	Reciprocal of resistance	Ohm^{-1} or Siemen	$S = AV^{-1}$
Frequency	Cycles/sec	Hertz	$Hz = s^{-1}$

* Newton is defined as the force which gives an acceleration of 1 m s^{-2} to a mass of 1 kg; so that

$f = ma = 1\ (1\ kg)\ (1\ m\ s^{-2}) = 1\ kg\ m\ s^{-2} = 1\ N$

** Joule is the work done when a displacement of 1 metre takes place by a force of 1 newton so that

$w = f \times d = (1N) \times (1\ m) = (1\ kg\ m\ s^{-2}) \times (1m) = 1\ kg\ m^2\ s^{-2} = 1\ J$

KEY NOTES

SOME IMPORTANT NOTES ON THE USE OF SI UNITS

In order to avoid confusion in the SI units, it is useful to remember the following points :

- Unit combinations should be indicated by means of either a dot or leaving space in between, *e.g.* metre kelvin may be written as :
  metre Kelvin = m.K or m K
  It should not be written as mK which stands for milli kelvin.
- Words and symbols should not be used in mixed forms. Thus, it is not proper to use J per mole. It should be written either as joule per mole or J mol^{-1}. *If mathematical operations are shown, only symbols should be used e.g.,* J mol^{-1} and not joule mol^{-1}.
- Symbols of the units do not have a plural ending like 's'. For example, we should write 10 cm and not 10 cms.
- A unit written with a prefix and a power is a power for the complete unit *e.g.,* cm^3 means $(centimetre)^3$ and not centi $(metre)^3$.
- Exponents also operate on prefixes. *e.g.,*
  $1\ cm^2 = (10^{-2}\ m)^2 = 10^{-4}\ m^2$
  $(\because\ 1\ cm = 10^{-2}\ m)$
  It is not equal to $10^{-2}\ m^2$
  Similarly,
  $1\ mm^3 = (10^{-3}\ m)^3 = 10^{-9}\ m^3$
  $(\because\ 1\ mm = 10^{-3}\ m)$
  It is not equal to $10^{-3}\ m^3$

It may be noted that some of the units are named after the name of the scientist who did pioneering work in the related field. For example, the unit of energy is joule abbreviated as 'J' and the unit of electric charge is coulomb abbreviated as C. *The symbols of the units which bear the names of the scientists are generally written in capital letters.* For example, the unit 'joule' is adopted after the name James P. Joule and is denoted by 'J' (capital J).

MEASUREMENT AND SIGNIFICANT FIGURES

Chemistry is largely an experimental science and deals with things that can be measured. A number of common devices are used in laboratories to make simple measurements. For example, a meter rod measures *length*, balance measures *mass;* burette, pipette, graduated cylinder and volumetric flask measure *volume;* thermometer measures *temperature,*

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etc. Every scientific measurement is limited by the reliability of the measuring instrument and the skill of the observer. In each measurement, uncertainty should be reported carefully. If we repeat a particular measurement, we usually do not obtain the same result because each measurement is subject to experimental error. Therefore, different measured values vary slightly from one another. To express the results of different measurements two terms ; accuracy and precision are commonly used.

Accuracy and Precision

The term accuracy denotes the closeness of an experimental value or the mean value of a set of measurements to the true value. Thus,

accuracy is a measure of the difference between the experimental value or the mean value of a set of measurements and the true value.

If the mean value of different measurements is close to the true value, the measurement is said to be **accurate**. Smaller the difference between the mean value and the true value, the larger is the accuracy. Suppose a sample of a compound contains 20.30% of chloride. The chemical analysis of the sample by one method (say method A) gives mean value of 20.60% chloride while another method (say method B) gives mean value of 20.46% chloride. Then,

Difference between the true value and mean value in method A = 20.60 – 20.30 = 0.30%

Difference between the true value and mean value in method B = 20.46 – 20.30 = 0.16%

Therefore, the method B gives more accurate data than method A. Thus, **accuracy also expresses the correctness of measurement.**

However, it may be noted that quite often, the true value of a quantity is not known. Therefore, it becomes very difficult to calculate the accuracy. In such cases, precision of the measurements is calculated.

Precision *refers to how closely two or more measurements of the same quantity agree with one another. Thus,*

precision is expressed as the difference between a measured value and the arithmetic mean value for a series of measurements.

In other words, precision gives the extent of agreement of the individual values among themselves *i.e.,* between the repeated measurements of the same quantity. *This means that smaller the difference between the individual values of repeated measurements, the greater is the precision.* For example, the analysis of an element gave the following results by two methods.

Method A : %Cl = 20.60 ± 0.05

Method B : %Cl = 20.46 ± 0.15

Thus, method A gives more precise data because the results differ only by ± 0.05%.

The terms accuracy and precision can be illustrated by the following example. Consider the results obtained by four students for the % of iron in a sample. These are given in Table 5 and are shown graphically in Fig. 7. The true value is 20.50 mg of iron.

Table 5. Results obtained by four students for the percentage of iron in a sample.

	Student A	Student B	Student C	Student D
	20.50	20.75	20.20	20.20
	20.48	20.65	20.25	20.40
	20.52	20.40	20.15	20.00
	20.50	20.28	20.20	20.60
Mean =	**20.50**	**20.52**	**20.20**	**20.30**
Deviation =	**± 0.02**	**± 0.24**	**± 0.05**	**± 0.30**

The results obtained by student A have good precision because the individual measurements are close together (± 0.02) and also have good accuracy because the mean result is same as the true value. The results of student B have low or poor precision because the measurements are scattered (± 0.24) but have good accuracy because the mean value (20.52) is close to the true value. Student C has obtained results of good precision because the measurements are close together (± 0.05) but have poor accuracy because the mean value (20.20) is far from the true value. The results of student D have poor precision because the measurements are scattered and have poor accuracy

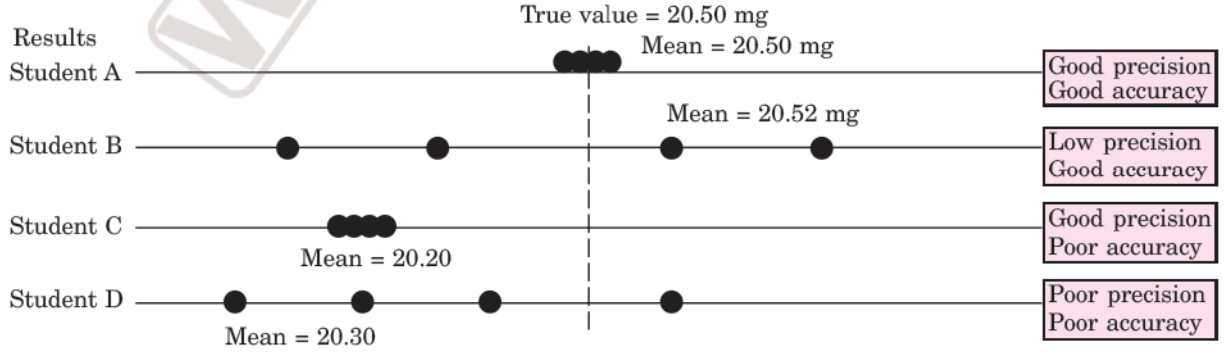

Fig. 7. Illustration of difference between accuracy and precision.

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because the mean value (20.30) is far from the true value.

From the above observation, it can be concluded that accurate results are generally precise but precise results need not be accurate. In other words, ***good precision does not assure good accuracy.***

Exponential Number or Scientific Notation.

In Chemistry, we come across very large and very small numbers. It is very tedious to write down such numbers in the ordinary way. For example, it is not convenient to write Avogadro constant as 602, 213, 700,000,000,000,000,000. These numbers are usually expressed in a simple way known as *exponential form* or *scientific notation*. For example, the number 246.38 may be expressed as :

$246.38 = 2.4638 \times 10 \times 10$ or $= 2.4638 \times 10^2$

where 10^2 means 10×10 and 2 is the power or exponent to which 10 is raised.

In general, in scientific notation, a number may be expressed as :

$$N \times 10^n$$

where n is an exponent having positive or negative values and N is a single non-zero digit and lies between 1 to 10. N is called **digit term** and n is called **exponent**.

For example, 1487.2 may be written as:

$1487.2 = 1.4872 \times 10 \times 10 \times 10 = 1.4872 \times 10^3$

In a simple way, the decimal point is moved to the left until there is only one **non zero** digit before the decimal point. If the decimal point is moved x places, the exponent $n = x$. For example, in transforming 1487.2 to scientific notation, the decimal point is moved to left three places as :

1487.2

Here exponent, $n = 3$ and we can write

$$1487.2 = 1.4872 \times 10^3$$

Similarly, Avogadro number, may be expressed as :

$602, 213,700,000,000,000,000,000 = 6.022137 \times 10^{23}$

Similarly, 0.00014872 may be written as:

$$0.00014872 = \frac{1.4872}{10 \times 10 \times 10 \times 10} = 1.4872 \times 10^{-4}$$

Here the exponent $n = -4$ means that the number 1.4872 has been divided by 10 four times. In a simple way, the decimal point is moved to the right until there is one non-zero digit before the decimal point. If the decimal point is moved y places, the exponent $n = -y$. For example, in transforming 0.00014872 to scientific notation, the decimal point is moved to right four places as :

0.0001 4872

so that exponent $n = -4$ and we can write

$$0.00014872 = 1.4872 \times 10^{-4}$$

Thus, in general, number is written in scientific notation as :

number with a single non-zero digit — number of places decimal point was moved

$N \times 10^n$

+ moved left

– moved right

Arithmetics Using Scientific Notation, Addition and Subtraction

To add or subtract numbers in scientific notation, the exponent (n) must be the same in both numbers. If the exponent is not same in both numbers, it has to be made same before adding or subtracting. For example, suppose we want to add 4.236×10^4 and 3.582×10^3. We must first express both numbers so that they have the same exponent, n. So we can transform 3.582×10^3 to 0.3582×10^4 and then add

$$4.236 \times 10^4 + 0.3582 \times 10^4 = (4.236 + 0.3582) \times 10^4$$
$$= 4.5942 \times 10^4$$

Similarly, to subtract these numbers,

$4.236 \times 10^4 - 3.582 \times 10^3$

$$4.236 \times 10^4 - 0.3582 \times 10^4 = (4.236 - 0.3582) \times 10^4$$
$$= 3.8778 \times 10^4$$

KEY NOTE

Before adding or subtracting scientific numbers, it is important to make both numbers to the same power of 10.

Multiplication and Division

To multiply two numbers in scientific notation, we make use of the relation :

$$(10)^x \times (10)^y = 10^{(x+y)}$$

In other words, we add the exponents. For example,

$$(2.4 \times 10^3) \times (5.6 \times 10^5) = (2.4 \times 5.6) \times 10^{3+5}$$
$$= 13.44 \times 10^8$$
$$(3.025 \times 10^3) \times (6.217 \times 10^{-6}) = (3.025 \times 6.217) \times 10^{3+(-6)}$$
$$= 18.81 \times 10^{-3} = 1.881 \times 10^{-2}$$
$$(9.8 \times 10^{-2}) \times (2.5 \times 10^{-6}) = (9.8 \times 2.5) \times 10^{-2+(-6)}$$
$$= 24.50 \times 10^{-8} = 2.450 \times 10^{-7}$$

To divide two numbers in scientific notation, we make use of the relation :

$$\frac{10^x}{10^y} = 10^{x-y}$$

In other words, we subtract the power of 10 of the number in the denominator from the power of 10 of the number in the numerator. For example,

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$$\frac{4.74 \times 10^{12}}{6.82 \times 10^{20}} = \left(\frac{4.74}{6.82}\right) \times 10^{12-20}$$
$$= 0.695 \times 10^{-8} = 6.95 \times 10^{-9}$$
$$\frac{2.7 \times 10^{-3}}{5.5 \times 10^{4}} = \left(\frac{2.7}{5.5}\right) \times 10^{-3-4}$$
$$= 0.4909 \times 10^{-7} = 4.909 \times 10^{-8}$$

Significant Figures

The uncertainty in the experimental or the calculated values is mainly due to the skill and accuracy of the observer and limitation of the measuring instrument as explained below:

(*i*) **Skill and accuracy of the observer.** Suppose three students A, B and C measure the volume of the liquid in a cylinder. They report the following values :

Result of A = 23.4 mL ; Result of B = 23.5 mL ;
Result of C = 23.6 mL

If the correct volume of the liquid is 23.5 mL, it means that the student B has measured the volume of the liquid *correctly* while the students A and C have made some error.

(*ii*) **Limitations of the measuring instrument.** Limitation of the measuring instrument is an important factor which leads to uncertainty in measurement. For example, suppose the mass of an object has been determined to be 9.265 g. If the accuracy of the analytical balance used is 0.001 g, this means that the actual mass of the object is 9.265 ± 0.001 g, i.e., it may be 9.264g or 9.266 g. Thus, in the reported mass, the first three digits (9, 2 and 6) are certain but the last digit(s) is uncertain and the uncertainty would be ±1 in the last digit. All measured quantities are reported in same way by writing the certain digits and the last uncertain digit. This is done in terms of *significant figures.*

The significant figures in a number are all the certain digits plus one uncertain digit.

For example, in the above value (9.265 g), there are four **significant figures**.

Thus, *the* ***number of significant figures conveys the information that except the last digit, all other digits are known with certainty.***

Rules for Determining the Number of Significant Figures

The following rules are followed to count the number of significant figures in a particular number :

(*i*) *All non-zero digits are significant.* For example,
3.132 has **four** significant figures
1.76 has **three** significant figures
5.4 has **two** significant figures
6.2316 has **five** significant figures.

The decimal place does not determine the number of significant figures.

(*ii*) *Zeros between two non zero digits* are significant. For example,
3.01 has **three** significant figures
2.005 has **four** significant figures
3.0023 has **five** significant figures

(*iii*) *The zeros preceding to the first non-zero number (i.e., to the left of the first non-zero number) are not significant.* Such zeros indicate the position of decimal point. For example,
0.324 has **three** significant figures
0.0052 has **two** significant figures
0.0003 has **one** significant figure

(*iv*) *All zeros placed at the end* or *to the right of a number are significant provided they are on the right side of the decimal point.* In fact, these represent the accuracy or the precision of the measuring scale. For example,
0.0200 has **three** significant figures
243.0 has **four** significant figures
243.00 has **five** significant figures
243.000 has **six** significant figures

KEY NOTE

- The results obtained by counting are **exact numbers** *i.e.,* numbers without any uncertainty. These exact numbers have infinite number of significant figures. For example, in 2 balls or 20 eggs, there are infinite number of significant figures because these are exact numbers and may be represented by writing infinite number of zeros after placing a decimal i.e. 2 = 2.000000 or 20 = 20.000000.
- Zeros at the end of a number or right of a number are significant provided they are on the right side of decimal point. For example, 0.300 has **three** significant figures. But zeros at the end of a number without decimal point are ambiguous. For example, 2500 may have two, three or four significant figures depending upon whether the uncertainty in measurements is 100, 10 or 1 respectively.

Exponential Numbers and Significant Figures

In exponential notations, the numerical portion (all digits) represents the number of significant figures. For example, a number, 0.000054 is expressed as 5.4×10^{-5} in terms of scientific notation. The number of significant figures in this number is **2**. Similarly, the number of significant figures in the Avogadro's number, 6.023×10^{23} is **four.**

Now, if we want to write five thousand with three significant figures, it can be written as

5.00×10^{3} (3 significant figures)

It cannot be written as 5000 because it has *four* and not three significant figures.

It must be **remembered** that the *decimal point does not count towards the number of significant figures.*

For example, consider the number 54023. It has five significant figures. We may write this number in different ways as:

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54.023 cm
5.4023 decimetre
or 0.54023 metre

All these numbers have the same number of significant figures (*i.e.*, 5) regardless of the position of the decimal point. The different numbers simply represent different ways (or units) of expressing the measurement.

The above rules for calculating significant figures are illustrated below :

Significant
0.000 2040 **4 significant figures**
Not significant

123.56 : 5 significant figures
5.407 : 4 significant figures (*zero is significant*)
900.0 : 4 significant figures (*all zeros are significant*)
0.0230 : 3 significant figures (*only last zero is significant*)

SOLVED EXAMPLES

Example 1.

State the number of significant figures in each of the following numbers :

(i) 207.35 (ii) 0.00368 (iii) 653
(iv) 3.653×10^4 (v) 0.378.

Solution:

(*i*) 207.35 has **five** significant figures.
(*ii*) 0.00368 has **three** significant figures. The three zeros in the beginning are not significant.
(*iii*) 653. It has **three** significant figures.
(*iv*) 3.653×10^4. It has **four** significant figures. The number has been expressed in scientific notation.
(*v*) 0.378 has **three** significant figures.

Example 2.

Express the following in the scientific notation :

(*i*) 0.0048 (*ii*) 234,000
(*iii*) 8008 (*iv*) 500.0
(*v*) 6.0012 ***N.C.E.R.T.***

Solution:

(*i*) $0.0048 = 4.8 \times 10^{-3}$
(*ii*) $234{,}000 = 2.340 \times 10^5$
(*iii*) $8008 = 8.008 \times 10^3$
(*iv*) $500.0 = 5.000 \times 10^2$
(*v*) $6.0012 = 6.0012$ or 6.0012×10^{-0}

Example 3.

Calculate the number of significant figures in the following values :

(*a*) *Planck's constant* $= 6.626 \times 10^{-34}$ *Js*
(*b*) *Avogadro number* $= 6.023 \times 10^{23}$
(*c*) *Velocity of light* $= 3.0 \times 10^8$ *m* s^{-1}
(*d*) *Electronic charge* $= 1.602 \times 10^{-19}$ *C*

Solution:

(*a*) 6.626×10^{-34} J s = 4 significant figures
(*b*) 6.023×10^{23} = 4 significant figures
(*c*) 3.0×10^8 m s^{-1} = 2 significant figures
(*d*) 1.602×10^{-19} C = 4 significant figures.

Example 4.

Calculate the number of significant figures in the following

(*i*) 0.0025 (*ii*) 208 (*iii*) 5005
(*iv*) 126,000 (*v*) 500.0 (*vi*) 2.0034

N.C.E.R.T.

Solution:

Number of significant figures :

(*i*) 0.0025 = 2
(*ii*) 208 = 3
(*iii*) 5005 = 4
(*iv*) 126000 = 3 (last three zeros are not significant)
(*v*) 500.0 = 4
(*vi*) 2.0034 = 5

Calculations Involving Significant Figures

The results of various measurements are to be added, subtracted, multiplied or divided, in most of the experiments to get desired results. But the different numbers do not have the same precision in measurement. In such cases, *the final result cannot be more precise than the least precise number involved in the calculations.* The number of the significant figures in such mathematical treatments are obtained by the following rules :

Rule 1. ***When addition or subtraction is to be carried out, the final result should be reported upto the same number of decimal places as are present in the term having the least number of decimal places.***

(*a*) **Addition of numbers.** In the addition of numbers 7.23, 2.1 and 0.312, the number having the least decimal places is 2.1. Therefore, the final result after adding should also have digits only up to one decimal place.

7.23
2.1 ⟵ has only one decimal place
0.312
9.642 ⟵ answer should be reported upto one decimal place.

Correct answer = **9.6**

Some more examples of addition of numbers are :

89.232
+ 1.1
90.332

Since 1.1 has one decimal place, therefore, answer should be reported to one decimal place.

Correct answer **= 90.3**

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7.21 12.141 0.0028 19.3538 Correct answer = **19.35**	Since 7.21 has two decimal places, therefore, answer should be reported upto two decimal places.

(*b*) **Subtraction of numbers.** The subtraction of numbers is carried out in the same way as the addition. For example :

25.4630
−24.21 ←——— has two decimal places
1.2530

Correct answer = **1.25** (upto two decimal places)

Some other examples are :

18.4215 − 6.0 12.4215	5.2748 − 5.2721 0.0027
Since 6.0 has only one digit after decimal Correct answer = **12.4**	Correct answer = **0.0027**

Rule 2. In multiplication or division, the final result should be reported up to the same number of significant figures as are present in the term with the least number of significant figures.

(*c*) **Multiplication of numbers.** If we multiply 5.1028 (having five significant figures) with 1.30 (having three significant figures), the value comes out to be 6.63364. But according to the rule, it must be reported with *three significant figures.* Therefore, the correct answer is 6.63.

5.1028 × 1.30 (3 significant figures)
= 6.63364

Correct answer = **6.63** (3 significant figures)

(*d*) **Division of numbers.** If we divide 5.2765 (having five significant figures) by 1.25 (having three significant figures), the result comes out to be 4.2212. But according to the rule, it must be reported with three significant figures. Thus, the correct answer is 4.22.

5.2765 ÷ 1.25
(3 significant figures)
= 4.2212

Correct answer = **4.22** (3 significant figures)

KEY NOTE

Calculations involving exact numbers

Exact numbers arise when we count items or **sometimes when we define a unit.** For example, when we say 10 pencils, we exactly mean 10, not 9.9 or 10.1. Also when we say that there are 12 inches in a foot, we mean exactly 12. **It may be noted that in calculations, the exact numbers will not have any effect on the number of significant figures.** The number of significant figures in a calculation result depends only on the numbers of significant figures in quantities having uncertainties. For example, we want to calculate the total mass of 8 pencils when each pencil has a mass of 3.0 g. The calculation is 3.0 × 8 = 24

Since 3.0 has two significant figures, the result should be 24 having two significant figures. The number 8 is exact and does not determine the number of significant figures.

It may be noted that **if a calculation involves a number of steps, the result should contain the same number of significant figures as that of the least precise number involved, other than the exact numbers.**

Retention of Significant Figures–Rounding off Figures

In solving problems, the final result often contains more digits than the number of significant figures. To retain the required number of significant figures, *rounding off* procedure is applied.

Rules for Rounding Off

(*i*) *If the digit coming after the desired number of significant figures happens to be more than 5, the preceding number is increased by 1.* For example, if we have to remove 6 in 1.386, we have to round it to 1.39.

(*ii*) *If the digit coming after the desired number of significant figures is less than 5, it is neglected as such i.e.,* the preceding number remains unchanged. For example, if we have to remove 4 in 6.234, we have to round it to 6.23.

(*iii*) *If the digit coming after the desired number of significant figures happens to be 5, then the preceding number is increased by 1 only in case it happens to be odd. In case of even number, the preceding number remains unchanged* For example, if 6.75 is to be rounded off by removing 5, we have to increase 7 to 8 giving 6.8 as the result. However, if 6.45 is to be rounded off, it is rounded off to 6.4.

Thus, to express the results to three significant figures

8.312 is rounded off to **8.31**
8.316 is rounded off to **8.32**
8.375 is rounded off to **8.38** [rule (*iii*)]
8.365 is rounded off to **8.36** [rule (*iii*)]

It must be **remembered** that if the problem involves more than one step, the 'rounding off' must be done only in the final answer. The intermediate steps of the calculations remain unchanged.

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SOLVED EXAMPLES

Example 5.

Express the following numbers up to four significant figures :

(i) 5.607892 *(ii) 32.392800*

(iii) 0.007837 *(iv) 1.78986×10^3*

(v) 60000

Solution:

(i) 5.607892 = **5.608** (ii) 32.392800 = **32.39**

(iii) 0.007837 = **0.007837**

(iv) 1.78986×10^3 = **1.790×10^3**

(v) 6.000×10^4

Example 6.

Express the following up to three significant places :

(a) the height of a man, 5 feet 9 inches in centimetres (1 inch = 2.54 cm)

(b) one millionth of one.

(c) four thousand

(d) decimal equivalent of 2/3

Solution:

(a) 5 ft 9 inches = 69 inch = $69 \times 2.54 = 175.26$ cm. With three significant figures answer is **175 cm.**

(b) One millionth of one is $\frac{1}{10^6}$. It can be written with 3 significant figures as **1.00×10^{-6}.**

(c) four thousand = **4.00×10^3**

(d) $\frac{2}{3}$ = **0.667.**

Example 7.

Calculate to proper significant figures :

(a) 12.6×11.2 *(b) 108/7.2*

Solution:

(a) $12.6 \times 11.2 = 141.12$

Correct answer = **141** (upto 3 significant figures)

(b) $\frac{108}{7.2} = 15$

Correct answer = **15** (upto 2 significant figures as in 7.2 (leaving exact number).

Example 8.

How many significant figures should be present in the answer of the following calculations ?

(i) $\frac{0.02856 \times 298.15 \times 0.112}{0.5785}$

(ii) 5×5.364

(iii) 0.0125 + 0.7864 + 0.0215 **N.C.E.R.T.**

Solution:

(i) $\frac{0.02856 \times 298.15 \times 0.112}{0.5785}$ = 3 significant figures

The number of significant figures, in 0.112 (least number of significant figures) is 3, therefore, the result should have **3 significant figures.**

(ii) 5×5.364 = **4 significant figures**

5.364 has four significant figures (leaving the exact number 5)

(iii) 0.0125 + 0.7864 + 0.0215 = 4 significant figures

The result is to be reported upto four decimal places as :

$$\begin{array}{r} 0.0125 \\ 0.7864 \\ 0.0215 \\ \hline 0.8204 \end{array}$$

it has **4 significant figures.**

Example 9.

Express the results of the following calculations to the appropriate number of significant figures :

(i) $\frac{3.24 \times 0.08666}{5.006}$ *(ii)* $\frac{(1.36 \times 10^{-4})(0.5)}{2.6}$

(iii) 0.582 + 324.65 *(iv)* $2.64 \times 10^3 + 3.27 \times 10^2$

(v) 943 × 0.00345 + 101.

Solution:

(i) $\frac{3.24 \times 0.08666}{5.006} = 0.05608$ = **0.0561**

In the calculation, the number of significant figures in the term 3.24 is 3, therefore, the result should have 3 significant figures. Therefore, the correct answer is **0.0561.** The number after 0 is 8 and therefore it is rounded off to 1.

(ii) $\frac{(1.36 \times 10^{-4})(0.5)}{2.6} = 0.2615 \times 10^{-4}$

= **0.3×10^{-4}.**

The answer should have one significant figure because 0.5 has one significant figure.

(iii)
$$\begin{array}{rr} & 0.582 \\ + & 324.65 \\ \hline & 325.232 \end{array}$$
(Second place of decimal)

= **325.23**

Since 324.65 contains digits up to second place of decimal, therefore, the answer must be reported up to second place.

(iv) $2.64 \times 10^3 + 3.27 \times 10^2$

or $2.64 \times 10^3 + 0.327 \times 10^3 = 2.967 \times 10^3$ = **2.97×10^3**

Since 2.64 has two digits after decimal place, the answer should be rounded off to two decimal places.

(v) The first two numbers are to be multiplied initially as follows :

$943 \times 0.00345 = 3.25335$ = **3.25.**

According to the rules on multiplication of significant figures, the answer has to be reported up to three significant figures. It should be 3.25. Upon further addition, the final answer may be calculated as :

$$\begin{array}{rr} & 3.25 \\ + & 101. \\ \hline & 104.25 \end{array}$$
(zero place of decimal)

= **104**

∴ The answer should have zero place of decimal.

Example 10.

The mass of a piece of paper is 0.02 g and the mass of a solid substance and the piece of paper is 20.036 g. If the volume of the solid is 2.16 cm^3, calculate the density of the substance up to proper number of significant digits.

Solution:

Mass of piece of paper = 0.02 g

Mass of solid substance and piece of paper = 20.036 g

∴ Mass of solid substance = $\begin{array}{r} 20.036 \\ -\ 0.02 \\ \hline 20.016 \end{array}$

or = 20.02 (upto second decimal place).

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Volume of solid = 2.16 cm^3

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{20.02}{2.16} = 9.268$$

Since 2.16 has three significant figures, the answer should also contain three significant figures.

∴ Density up to proper number of significant figures = **9.27 g/cm^3.**

❑ Example 11.

Perform the following calculations and express the result to proper number of significant figures :

(i) 144.3 m^2 + (2.54 m × 8.4 m)

(ii) (4.05 × 10^2 mL) – (0.0225 × 10^2 mL)

(iii) (3.50 × 10^2 cm) (4.00 × 10^6 cm)

Solution:

(*i*) (144.3 m^2) + (2.54 m × 8.4 m)

2.54 m × 8.4 m = 21.336 m^2 or 21 m^2 (upto 2 significant figures)

144.3 m^2
21.0 m^2
———————
165.3 m^2 or **165 m^2**

(*ii*) (4.05 × 10^2 mL) – (0.0225 × 10^2 mL)

4.05 × 10^2 mL
– 0.0225 × 10^2 mL
———————————
4.0275 × 10^2 mL or **4.03 × 10^2 mL** (upto second decimal place as in 4.05)

(*iii*) (3.50 × 10^2 cm) × (4.00 × 10^6 cm)
= 14.0 × 10^8 cm^2(upto 3 significant figures)

Practice Problems

1. Calculate the number of significant figures in the following :
(*a*) 1.00 × 10^6 (*b*) 0.0050 (*c*) 1.234
(*d*) 0.0006 (*e*) 0.368

2. Express the following numbers to three significant figures :
(*i*) 6.023 × 10^{23} (*ii*) 6000 (*iii*) 32.362400
(*iv*) 5.6034 (*v*) decimal equivalent of 2/3
(*vi*) 1.6276 × 10^4

3. The density of ice is 0.921 g cm^{-3}. Calculate the mass of a cubic block of ice which is 76 mm on each side.

4. Express the following numbers in exponential notations to three significant figures :
(*i*) 900035 (*ii*) 0.000002136
(*iii*) 406721 (*iv*) 0.000001

5. Perform the following calculations to proper number of significant figures :
(*a*) 108/7.2 (*b*) $(1.6 \times 10^2)^2$

(*c*) $\dfrac{(1.35 \times 10^{-6})(0.4)}{5.6}$ (*d*) $\dfrac{3.25 \times 0.08621}{4.002}$

(*e*) (1.0042 – 0.0034) (1.23)

6. Calculate
(*i*) area of a square whose side is 1.2 m
(*ii*) volume of a sphere whose radius is 1.6 cm
(*iii*) length of a rectangle having area 10.25 m^2 and breadth 2.5 m.

7. Perform the following calculations upto proper number of significant figures :
(*i*) $(1.20 \times 10^{-6}) + (6.00 \times 10^{-5}) = ?$
(*ii*) $(2.164 \times 10^5)^{\frac{1}{2}} = ?$
(*iii*) $(9.13 \times 10^{-2})(7.006 \times 10^{-3}) = ?$
(*iv*) $4.00 \times 10^{-2} + 3.26 \times 10^{-3} + 1 \times 10^{-6} = ?$

8. Calculate the number of significant figures up to which the following results will be expressed :

(*i*) $\dfrac{2.36 \times 0.07251}{2.130}$ (*ii*) $\dfrac{(28.2 - 21.2)(1.79 \times 10^6)}{1.62}$

9. Round up the following upto three significant figures :
(*i*) 34.216 (*ii*) 10.4107
(*iii*) 0.04597 (*iv*) 2808

10. If the speed of light is 3.0 × 10^8 ms^{-1}, calculate the distance covered by the light in 2.00 ns.

Answers to Practice Problems

1. (*a*) Three (*b*) Two (*c*) Four (*d*) One (*e*) Three
2. (*i*) 6.02 × 10^{23} (*ii*) 6.00 × 10^3 (*iii*) 32.4 (*iv*) 5.60 (*v*) 0.667 (*vi*) 1.63 × 10^4
3. 4.0 × 10^2 g
4. (*i*) 9.00 × 10^5 (*ii*) 2.14 × 10^{-6} (*iii*) 4.07 × 10^5 (*iv*) 1.00 × 10^{-6}
5. (*a*) 15 (*b*) 2.6 × 10^4 (*c*) 1 × 10^{-7} (*d*) 0.0700 (*e*) 1.23
6. (*i*) 1.4 m^2 (*ii*) 17 cm^3 (*iii*) 4.1 m
7. (*i*) 6.12 × 10^{-5} (*ii*) 4.652 × 10^2 (*iii*) 6.40 × 10^{-4} (*iv*) 4.33 × 10^{-2}
8. (*i*) Three (*ii*) Two
9. (*i*) 34.2 (*ii*) 10.4 (*iii*) 0.0460 (*iv*) 2.81 × 10^3
10. 0.60m

Hints & Solutions on page 79

DIMENSIONAL ANALYSIS

Conversion of Units

It is frequently necessary to convert one set of units to another in calculations. This can be done by a method called **factor label method** or **unit factor method** or also called **dimensional analysis.** This is based on the relationship between different units that expresses the same quantity. For example, suppose we want to convert 25.6 metres to centimetres. We know that

1 m = 100 cm

or $1 = \dfrac{100 \text{ cm}}{1 \text{ m}}$

100 cm/1 m is called *unit conversion factor* or *conversion factor* because *it converts a quantity expressed in one unit to a quantity expressed in another unit.* It is also called *unit factor* because the overall effect of multiplication by these factors is to multiply by 1.

Now, multiply the given quantity by the conversion factor, retaining the units of the physical quantity and that of the conversion factor in such a way that all units cancel out leaving behind only the required units i.e., numerator should have that part which is required in the desired result.

Thus, 25.6 m = 25.6 ~~m~~ × $\dfrac{100 \text{ cm}}{1 \text{ ~~m~~}}$ = 2560 cm.

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- ***It may be remembered that we choose the conversion factor that has metres in the denominator.***

The advantage of this method is that if the equation is set up correctly, only then all the units will get cancelled except the required unit. If we do not get desired unit, then an error must have been made.

Let us consider another example. Suppose we want to convert 1.50 km^3 of water into volume in litres. We know that

$$1L = 1\ dm^3$$

So, we want to convert km^3 to dm^3 (litres). This can be done in two steps as :

(*i*) Convert km^3 to m^3

(*ii*) Convert m^3 to dm^3

For converting km^3 to m^3, the unit factor is

$$1\ km = 10^3\ m$$

so that $$1 = \left(\frac{10^3 m}{1\ km}\right)$$

$$\therefore \quad 1.50\ km^3 = 1.50\ \cancel{km^3} \times \left(\frac{10^3 m}{1\ \cancel{km}}\right)^3$$

$$= 1.50 \times 10^9\ m^3$$

Now $$1\ m = 10\ dm$$

or $$1 = \frac{10\ dm}{1\ m}$$

Applying unit factor,

$$\text{Volume of water} = 1.50 \times 10^9\ \cancel{m^3} \times \left(\frac{10\ dm}{1\ \cancel{m}}\right)^3$$

$$= 1.50 \times 10^{12}\ dm^3$$

Both the steps can be performed in a single step as

$$\text{Volume of water} = 1.50\ \cancel{km^3} \times \underbrace{\left(\frac{10^3 m}{1\ km}\right)^3}_{\text{Converts km}^3 \text{ into m}^3} \times \underbrace{\left(\frac{10\ dm}{1\ m}\right)^3}_{\text{Converts m}^3 \text{ into dm}^3}$$

$$= 1.50 \times 10^{12}\ dm^3$$

Since cubic decimetre is equal to litres, the volume of water is

$$= 1.50 \times 10^{12} \text{ litres}$$

It should also be noted that units can be handled just like numerical part i.e., it can be cancelled, multiplied, divided, squared, etc.

Let us convert litre atmosphere to joule (the SI unit of energy). Let us convert 1 L atm to joules. This can be done by multiplying with two unit factors as :

$$1\ L = 10^{-3}\ m^3 \qquad \text{or} \qquad 1 = \left(\frac{10^{-3} m^3}{L}\right)$$

$$1\ atm = 101.325 \times 10^3\ Pa$$

$$\text{or } 1 = \frac{101.325 \times 10^3 Pa}{atm}$$

Applying these unit factors :

$$1\ L\ atm = \cancel{1\ L}\ \cancel{atm} \times \left(\frac{10^{-3} m^3}{\cancel{1L}}\right) \times \left(\frac{101.325 \times 10^3 Pa}{\cancel{atm}}\right)$$

$$= 101.325\ Pa\ m^3$$

Now, $$Pa = \frac{N}{m^2}$$

$$\therefore \quad 101.325\ Pa\ m^3 = 101.325 \left(\frac{N}{m^2}\right) m^3$$

$$= 101.325\ Nm$$

$$= 101.325\ J \qquad [\because Nm = J]$$

Thus, **1 L atm = 101.325 J**

Thus, we can easily apply several conversion factors in one step. For example, suppose we want to convert 2.50 miles into centimetres. The relationship between various units are :

1 mile = 1760 yards, 1 yard = 3 ft, 1 ft = 12 inches and 1 inch = 2.54 cm.

The unit factors are :

$$1 = \frac{1760\ yards}{1\ mile};\ 1 = \frac{3\ ft}{1\ yard};\ 1 = \frac{12\ inches}{1\ ft};$$

and $$1 = \frac{2.54\ cm}{1\ inch}$$

Applying these unit factors,

$$2.50\ \cancel{miles} \times \underbrace{\frac{1760\ \cancel{yards}}{1\ \cancel{mile}}}_{\text{Converts mile into yard}} \times \underbrace{\frac{3\ \cancel{ft}}{1\ \cancel{yard}}}_{\text{Converts yard into ft}} \times \underbrace{\frac{12\ \cancel{inches}}{1\ \cancel{ft}}}_{\text{Converts ft into inch}} \times \underbrace{\frac{2.54\ cm}{1\ \cancel{inch}}}_{\text{Converts inch into cm}}$$

$$= 402336\ cm$$

or $$= 4.02 \times 10^5\ cm$$

Table 6. Relation between various units.

Units of length	Units of mass	Units of volume
1 mile = 1760 yard	1 kg = 10^3 g	1 m^3 = 10^3 L
1 yard = 3 ft	1g = 1000 mg	1 dm^3 = 1 L
1 ft = 12 inch	1 lb = 453.59 g	1 cm^3 = 10^{-3} L
1 inch = 2.54 cm	1 oz = 28.35 g	1 ft^3 = 28.32 L
1 metre = 100 cm	1 metric ton = 1000 kg	1 quart = 0.9464 L
1 km = 1000 m	= 2205 lb	1 L = 1.056 quarts
1 mile = 1.609 km	1 g = 15.4 grains	
1 mile = 5280 ft	1 carat = 3.168 grains	

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Other units

1 Å = 10^{-10} m
1 atm = 760 mm or 760 torr
= 101,325 Pa or Nm^{-2}
= 1.013×10^6 dyne cm^{-2}
1 bar = 10^5 Nm^{-2} = 10^5 Pa
1 mm or 1 torr = 133.322 Pa or Nm^{-2}

1 dyne = 10^{-5} N
1 calorie = 4.184 J
1 erg = 10^{-7} J
1 eV = 1.6022×10^{-19} J

SOLVED EXAMPLES

Example 12.

The density of vanadium is 5.96 g cm^{-3}. Convert the density to SI units of kg m^{-3}.

Solution: Density = 5.96 g cm^{-3}

We know 1 kg = 1000 g

$\therefore$ *Unit factor* = $\frac{1\text{ kg}}{1000\text{ g}}$

1 m = 100 cm

$\therefore$ *Unit factor* = $\frac{100\text{ cm}}{1\text{ m}}$

Applying unit factor for g and cm^3, we get

$$\therefore 5.96\text{ g cm}^{-3} = \frac{5.96\,\text{g}}{\text{cm}^3} \times \frac{1\text{ kg}}{1000\,\text{g}} \times \left(\frac{100\,\text{cm}}{1\text{ m}}\right)^3$$

$$= 5.96 \times 10^3\text{ kg m}^{-3}$$

$$= \mathbf{5960\ kg/m^3.}$$

Example 13.

A jug contains 2 L of milk. Calculate the volume of milk in m^3. **N.C.E.R.T.**

Solution: We know

1 L = 1000 cm^3

or Unit factor = $\frac{1000\text{ cm}^3}{1\text{ L}}$

1 m = 100 cm

Unit factor = $\frac{1\text{ m}}{100\text{ cm}}$

$$\text{Volume of milk} = 2\,\text{L} \times \left(\frac{1000\,\text{cm}^3}{1\,\text{L}}\right) \times \left(\frac{1\text{ m}}{100\text{ cm}}\right)^3$$

$$= \mathbf{2 \times 10^{-3}\ m^3}$$

Example 14.

Express each of the following in S I units :

(i) 93 million miles (this is the distance between the earth and the sun).

(ii) 5 feet 2 inches (this is the average height of an Indian female).

(iii) 100 miles per hour (this is the typical speed of Rajdhani Express).

(iv) 0.74 Å (this is the bond length of hydrogen molecule).

(v) 46°C (this is the peak summer temperature in Delhi).

(vi) 150 pounds (this is the average weight of an Indian male). **N.C.E.R.T.**

Solution:

(i) The S I unit of distance is metre (m)

1 mile = 1.60 kilometre = 1.60 × 1000 m

Unit factor = $\frac{1.60 \times 1000\text{ (m)}}{1\text{ mile}} = \frac{1.6 \times 10^3\text{ (m)}}{1\text{ mile}}$

$\therefore$ 93 million miles = $\frac{93 \times 10^6\ (\text{miles}) \times 1.6 \times 10^3\text{ (m)}}{1\ \text{mile}}$

$= 93 \times 1.6 \times 10^9$ m

$= \mathbf{148.8 \times 10^9\ m = 1.49 \times 10^{11}\ m.}$

(ii) 5 feet 2 inches = 62 inches

1 inch = 2.54×10^{-2} m

Unit factor = $\frac{2.54 \times 10^{-2}\text{ (m)}}{1\text{ inch}}$

62 inches = $\frac{62\ (\text{inches}) \times 2.54 \times 10^{-2}\text{ m}}{1\ \text{inch}}$

$= 62 \times 2.54 \times 10^{-2}$ m

$= 157.48 \times 10^{-2}$ m = **1.57 m.**

(iii) 1 mile = 1.60 km = 1.60×10^3 m

Unit factor = $\frac{1.60 \times 10^3\text{ m}}{1\text{ mile}}$

1 hr = 60 × 60 s = 3.6×10^3 s

Unit factor = $\frac{3.6 \times 10^3\text{s}}{1\text{ hr}}$

$\therefore$ Speed = $\frac{100\text{ miles}}{\text{hr}}$

$$= \frac{100\,\text{miles}}{\text{hr}} \times \frac{1.60 \times 10^3\text{ m}}{1\,\text{mile}} \times \frac{1\,\text{hr}}{3.6 \times 10^3\text{s}}$$

$= \mathbf{44\ m\ s^{-1}}$.

(iv) 1 Å = 10^{-10} m.

Unit factor = $\frac{10^{-10}\text{ m}}{1\text{ (Å)}}$

$\therefore$ 0.74 Å = $\frac{0.74\,\text{Å} \times 10^{-10}\text{ (m)}}{1\,\text{(Å)}}$

$= 0.74 \times 10^{-10}$ m or = $\mathbf{7.4 \times 10^{-11}\ m}$

(v) 0°C = 273.15 K

46°C = 273.15 K + 46 K = **319.15 K**

(vi) 1 pound = 454×10^{-3} kg

Unit factor = $\frac{454 \times 10^{-3}\text{ (kg)}}{1\text{ (pound)}}$

$\therefore$ 150 pound = $\frac{150\ (\text{pound}) \times 454 \times 10^{-3}\text{ (kg)}}{1\ (\text{pound})}$

$= 150 \times 454 \times 10^{-3}$ kg = **68.1 kg.**

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Example 15.

The mass of precious stones is expressed in terms of 'carat'. What is the mass of a ring in grams which contains 0.600 carat diamond and 8.500 g gold given that 1 carat = 3.168 grains and 1 g = 15.4 grains ?

Solution:

Weight of ring = 0.600 carat diamond + 8.500 g gold

Now 1 carat = 3.168 grains

$$\text{Unit factor} = \frac{3.168 \text{ grains}}{1 \text{ carat}}$$

1 g = 15.4 grains

$$\text{Unit factor} = \frac{1 \text{ g}}{15.4 \text{ grains}}$$

Weight of diamond = 0.600 carat

$$= 0.600 \cancel{\text{carat}} \times \frac{3.168 \cancel{\text{grains}}}{1 \cancel{\text{carat}}} \times \frac{1 \text{ gram}}{15.4 \cancel{\text{grains}}}$$

$$= \mathbf{0.123\ g}$$

Total mass of ring = 8.500 + 0.123 **= 8.623 g**

Example 16.

A tennis ball was observed to travel at a speed of 96 miles per hour. Calculate the speed of the ball in metres per second.

Solution:

Speed of tennis ball = 96 miles per hour

Now 1 mile = 1.60 km = 1.60×10^3 m

$$\text{Unit factor} = \frac{1.60 \times 10^3 \text{ m}}{1 \text{ mile}}$$

1 hr = 60 × 60 s = 3.6×10^3 s

$$\text{Unit factor} = \frac{3.6 \times 10^3 \text{ s}}{1 \text{ hr}}$$

$$\therefore \quad \text{Speed} = \frac{96 \text{ mile}}{\text{hr}}$$

$$= \frac{96 \cancel{\text{mile}}}{\cancel{\text{hr}}} \times \frac{1.60 \times 10^3 \text{ m}}{1 \cancel{\text{mile}}} \times \frac{1 \cancel{\text{hr}}}{3.6 \times 10^3 \text{ s}}$$

$$= \mathbf{42.7\ m\ s^{-1}}$$

Example 17.

(a) Convert the following in kilogram

(i) 0.91×10^{-27} g (mass of electron)

(ii) 1 fg (mass of human DNA molecule)

(b) Convert into metre

(i) 1.4 Gm (diameter of Sun)

(ii) 40 Em (thickness of Milky Way Galaxy)

Solution: (a) (i) 0.91×10^{-27} g (mass of electron)

$1 \text{ g} = 10^{-3}$ kg

$$\text{or} \quad \text{Unit factor, } 1 = \frac{10^{-3} \text{ kg}}{1 \text{ g}}$$

$$\therefore \quad 0.91 \times 10^{-27} \text{ g} = 0.91 \times 10^{-27} \cancel{\text{g}} \times \left(\frac{10^{-3} \text{ kg}}{1 \cancel{\text{g}}}\right)$$

$$= 9.1 \times 10^{-31} \text{ kg}$$

(ii) Mass of human DNA molecule = 1 fg

$1 \text{ fg} = 10^{-15}$ g

$$\text{or} \quad \text{Unit factor, } 1 = \frac{10^{-15} \text{g}}{1 \text{ fg}}$$

$1 \text{ g} = 10^{-3}$ kg

$$\text{or} \quad \text{Unit factor, } 1 = \frac{10^{-3} \text{ kg}}{1 \text{ g}}$$

$$\therefore \quad 1 \text{ fg} = 1 \text{ fg} \times \left(\frac{10^{-15} \cancel{\text{g}}}{1 \cancel{\text{fg}}}\right) \times \left(\frac{10^{-3} \text{kg}}{1 \cancel{\text{g}}}\right)$$

$$= 1 \times 10^{-18} \text{ kg}$$

(b) (i) 1.4 Gm (diameter of Sun)

We know $1 \text{ Gm} = 10^9$ m

$$\text{or} \quad \text{Unit factor, } 1 = \frac{10^9 \text{m}}{1 \text{ Gm}}$$

$$\therefore \quad 1.4 \text{ Gm} = 1.4 \cancel{\text{Gm}} \times \left(\frac{10^9 \text{m}}{1 \cancel{\text{Gm}}}\right) = \mathbf{1.4 \times 10^9\ m}$$

(ii) 40 Em (thickness of Milky Way Galaxy)

We know, $1 \text{ Em} = 10^{18}$ m

$$\text{or Unit factor, } 1 = \frac{10^{18} \text{m}}{1 \text{Em}}$$

$$\therefore \quad 40 \text{ Em} = 40 \cancel{\text{Em}} \times \left(\frac{10^{18} \text{m}}{1 \cancel{\text{Em}}}\right) = \mathbf{40 \times 10^{18}\ m}$$

$$\text{or} \quad = \mathbf{4.0 \times 10^{19}\ m}$$

Practice Problems

11. The wavelength of a yellow line in spectrum of sodium atom is 5896 Å. Express it in nm.

12. How many cubic centimetres are there in 1 m^3 ?

13. Convert

(i) 4.86 kg/L to grams per millilitre

(ii) 1.86 km to cm

(iii) 6.92×10^{-7} m to micrometres and Angstroms

(iv) 9.2×10^{-3} cm^3 to litres

14. What is the capacity of a tank 0.8 m long 10 cm wide and 50 mm deep ?

15. How many cubic centimetres are there in 100 L ?

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16. Convert the following in kilogram :
(*i*) 500 Mg (mass of jumbo jet loaded)
(*ii*) 3.34×10^{-24} g (mass of hydrogen molecule)

17. Express the following in the designated units :
(*i*) 1.54 mm s^{-1} to pm μs^{-1}
(*ii*) 25 gL^{-1} to mg dL^{-1}
(*iii*) 25 L to m^3
(*iv*) 2.66 g cm^{-3} to $\mu g\ \mu m^{-3}$
(*v*) 4.2 Lh^{-2} to mL s^{-2}

18. Convert into metre :
(*i*) 7 nm (diameter of small virus)
(*ii*) 41 pm (distance of nearest star)

19. How many seconds are there in 2 days ?

N.C.E.R.T.

20. Convert the following into base units :
(*i*) 28.7 pm
(*ii*) 15.15 μs
(*iii*) 25365 mg

Answers to Practice Problems

11. 589.6 nm
12. 10^6 cm^3
13. (*i*) 4.86 g/mL (*ii*) 1.86×10^5 cm
(*iii*) 0.692 μm, 6920 Å (*iv*) 9.2×10^{-6} L
14. 4L
15. 10^5 cm^3
16. (*i*) 5.0×10^5 kg (*ii*) 3.34×10^{-27} kg
17. (*i*) 1.54×10^3 pm μs^{-1} (*ii*) 2.5×10^3 mg dL^{-1}
(*iii*) 2.5×10^{-2} m^3 (*iv*) 2.66×10^{-6} $\mu g\ \mu m^{-3}$
(*v*) 3.2×10^{-4} mL s^{-2}
18. (*i*) 7×10^{-9} m (*ii*) 41×10^{-12} m
19. 172800 s
20. (*i*) 2.87×10^{-11}m (*ii*) 1.515×10^{-5}s
(*iii*) 2.5365×10^{-2} kg

Hints & Solutions on page 79

LAWS OF CHEMICAL COMBINATION

In the seventeenth century, the scientists had been trying to find out methods for converting one substance into another. During their quantitative studies of chemical changes, they made certain generalisations. These generalisations are known as *laws of chemical combination*. These are :

1. Law of conservation of mass
2. Law of constant composition or definite proportions
3. Law of multiple proportions
4. Law of reciprocal proportions
5. Law of combining volumes (or Gay Lussac's law of combining volumes).

The first four laws of chemical combination deal with mass relationships while the fifth law deals with the volumes of the reacting gases.

1. Law of Conservation of Mass

This law deals with the relation between the *mass of reactants and the products during the chemical changes*. It was postulated by a French chemist Antoine Lavoisier in 1789.

Law of conservation of mass states that

during any physical or chemical change, the total mass of the products is equal to the total mass of the reactants.

In other words, ***matter can neither be created nor destroyed during any physical or chemical change.***

Therefore, this law is also known as **law of indestructibility of matter.**

Experimental verification of the law of conservation of mass.

The law can be verified with the help of *Landolt's* experiment. Landolt took the solutions of sodium chloride (NaCl) and silver nitrate ($AgNO_3$) separately in two limbs of a 'H' shaped tube (known as Landolt's tube). The tube was sealed and weighed. After weighing, the two solutions were mixed thoroughly by shaking the tube. As a result, the reaction occurred between silver nitrate and sodium chloride and a white ppt. of silver chloride is formed as:

$$AgNO_3(aq) + NaCl\ (aq) \longrightarrow \underset{\text{White ppt.}}{AgCl(s)} + NaNO_3(aq)$$

After the reaction, the tube was again weighed. It was observed that the weight remained practically unchanged. This verified the law of conservation of mass.

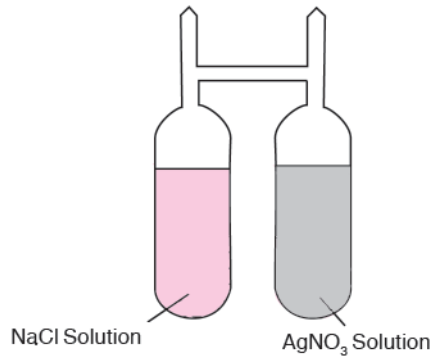

Fig. 8. Landolt's experiment.

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LEARNING PLUS

Present Position of the Law in the Light of Recent Developments

It may be noted that the law of conservation of mass is not strictly valid for nuclear reactions.

According to Einstein theory of relativity, mass and energy are interconvertible. The mass (m) and energy (E) are related as, $E = mc^2$ where c is the velocity of light (3×10^8 m/sec). We know that chemical reactions are generally accompanied by liberation of energy. Since energy and mass are related to each other, this means that the energy must be coming from the reactants. As a result, there should be decrease in mass of the reactants. However, the mass changing into energy for ordinary chemical reactions (according to relation $m = E/c^2$) is extremely small because the value of c is very large and, therefore, there is no measurable change in mass during chemical processes. However, in case of **nuclear reactions** and **radioactive disintegrations,** the change in mass is quite significant because tremendous amount of energy is released during these reactions. Therefore, the law of conservation of mass does not hold good. In these reactions, some mass gets converted into energy. In such cases, mass and energy is totally conserved though mass and energy are not separately conserved. Thus, law of conservation of mass is modified and the modified law is known as **law of conservation of mass-energy** which states that ***mass and energy are interconvertible, but the total mass and energy of the system remains constant.***

2. Law of Constant Composition or Definite Proportions

The law of constant composition deals *with the composition of various elements present in a compound.* It was stated by a French chemist, *Joseph Proust,* in 1799. **Law of constant composition** states that

a pure chemical compound always contains same elements combined together in the same definite proportion by weight.

Proust worked with two samples of cupric carbonate; one of which was naturally occurring cupric carbonate and other was prepared in the laboratory. He found that the composition of the elements present in two samples of cupric carbonate was same as shown below :

	Percentage		
	Cu	C	O
Naturally occurring cupric carbonate	51.35	9.74	38.91
Cupric carbonate prepared in laboratory	51.35	9.74	38.91

The above results show that irrespective of the source, a given compound always contains same elements in the same proportion. This law is sometimes referred to as law of **definite composition** or **definite proportion**.

Similarly, carbon dioxide can be obtained by a number of methods, such as

(*i*) By burning coal or candle

$$C + O_2 \longrightarrow CO_2$$

(*ii*) By heating limestone ($CaCO_3$)

$$CaCO_3 \xrightarrow{\text{Heat}} CaO + CO_2$$

(*iii*) By the action of dilute hydrochloric acid on marble pieces.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$

(*iv*) By heating sodium bicarbonate.

$$2NaHCO_3 \xrightarrow{\text{Heat}} Na_2CO_3 + CO_2 + H_2O$$

It has been observed that each sample of carbon dioxide contains carbon and oxygen elements in the ratio of 3 : 8 by weight.

Similarly, pure water can be obtained from many sources. Irrespective of the source, water always contains hydrogen and oxygen elements combined together in the ratio of 1 : 8 by weight.

Experimental verification of the law. The law can be easily verified in the laboratory. For example, copper oxide (CuO) can be prepared by the following methods :

(*i*) by heating copper powder in oxygen :

$$\underset{\text{Copper powder}}{2Cu} + O_2 \longrightarrow 2CuO$$

(*ii*) by heating copper carbonate :

$$\underset{\text{Copper carbonate}}{CuCO_3} \longrightarrow CuO + CO_2$$

(*iii*) by heating copper nitrate :

$$\underset{\text{Copper nitrate}}{2Cu(NO_3)_2} \longrightarrow 2CuO + 4NO_2 + O_2$$

The weighed quantities of three samples of copper oxide as obtained above were reduced to copper separately in a current of hydrogen :

$$CuO + H_2 \longrightarrow Cu + H_2O$$

The weight of copper left behind in each case is noted. From the weight of copper left behind, the weight of oxygen in the samples of copper oxides was calculated.

It was observed that in all the samples, the ratio of copper and oxygen by weight has been found to be the same *i.e.,* 4 : 1. This illustrates the law of constant composition.

Limitations of Law of Constant Composition

(*i*) The law of constant composition does not hold good when a compound is obtained by using different isotopes of the combining elements. For example, when CO_2 is formed from C-12 the ratio between C and O is 12 : 32. But when CO_2 is formed from C-14 isotope, the ratio of C : O is 14 : 32. Thus, *different isotopes of the same element give different mass ratio between combining atoms.*

(*ii*) The elements may combine in the same ratio but the compounds formed may be different.

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For example, in the compounds C_2H_5OH and CH_3OCH_3 (both have same molecular formula C_2H_6O, known as isomers) the ratio of C : H : O is 24 : 6 : 16 or 12 : 3 : 8. Thus, *the inverse of the law is not correct*.

3. Law of Multiple Proportions

This law was proposed by Dalton in 1803. **Law of multiple proportions** states that

when two elements combine to form more than one compound, then the masses of one of the elements which combine with a fixed mass of the other element are in a simple whole number ratio.

The law may be **illustrated** by the following examples :

(*i*) Hydrogen combines with oxygen to form two compounds namely *water* and *hydrogen peroxide*.

In water, 2 parts by mass of hydrogen combine with 16 parts by mass of oxygen as :

Hydrogen + Oxygen ⟶ Water
2 g 16 g 18g

In hydrogen peroxide, 2 parts by mass of hydrogen combines with 32 parts by mass of oxygen as :

Hydrogen + Oxygen ⟶ Hydrogen peroxide
2 g 32 g 34g

Therefore, the masses of oxgen (16 g, 32 g) which combine with fixed mass of hydrogen (2 parts) bear a simple ratio *i.e.* 16 : 32 or 1 : 2.

(*ii*) Nitrogen and oxygen combine to form five oxides namely nitrous oxide (N_2O), nitric oxide (NO), nitrogen trioxide (N_2O_3), nitrogen tetroxide (N_2O_4) and nitrogen pentoxide (N_2O_5). The different weights of oxygen which combine with the fixed weight of nitrogen in all these oxides are calculated.

Oxide	Number of parts by weight of nitrogen	Number of parts by weight of oxygen	Fixed weight of nitrogen (14 parts)	Number of parts by weight of oxygen combining with 14 parts by weight of nitrogen
N_2O	28	16	14	8
NO	14	16	14	16
N_2O_3	28	48	14	24
N_2O_4	28	64	14	32
N_2O_5	28	80	14	40

The ratio between the different weights of oxygen in different compounds which combine with the same weight of nitrogen (14 parts) is :

8 : 16 : 24 : 32 : 40
or 1 : 2 : 3 : 4 : 5

This is a simple whole number and hence, supports the law.

Experimental Verification of Law of Multiple Proportions

Copper forms two oxides cuprous oxide (Cu_2O) and cupric oxide (CuO). 1.00 gm of each oxide of copper (CuO and Cu_2O respectively) is heated in a current of hydrogen. Both the oxides react with hydrogen producing metallic copper. From the weight of copper obtained, the respective weights of oxygen in the two compounds are obtained. Then, the different weights of oxygen which combine with the same weight of copper in the two compounds are calculated. These weights are found to bear a simple whole number ratio. Thus, the law has been verified.

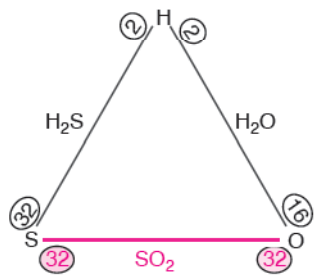
4. Law of Reciprocal Proportions or Law of Equivalent Proportions

This law was put forward by Richter in 1792. It states that

when two different elements combine separately with a fixed mass of a third element, the ratio in which they do so will be the same or some simple multiple of the ratio in which they combine with each other.

In other words, the mass ratio of two elements A and B which combine with the fixed mass of C separately, is either the same or some simple whole number multiple of the mass ratio in which A and B combine together. This law may be illustrated by the following examples :

Consider three elements sulphur, oxygen and hydrogen. Both sulphur and oxygen separately combine to form hydrogen sulphide (H_2S) and water (H_2O) respectively. They also combine with each other to form sulphur dioxide (SO_2) as shown:



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According to the law, the ratio of weights of S and O which combine with the same weight of H will either be same or a simple multiple of the ratio in which S and O combine with each other. This may be verified as :

In hydrogen sulphide (H_2S), 2 parts by weight of hydrogen combine with 32 parts by weight of sulphur.

In water molecule (H_2O), 2 parts by weight of hydrogen combine with 16 parts by weight of oxygen.

$\therefore$ The ratio of the weights of sulphur and oxygen which, combine separately with the fixed weight (= 2 parts) of hydrogen is,

$$32 : 16 \text{ or } 2 : 1 \qquad ...(i)$$

Now, let us calculate the ratio of sulphur and oxygen in SO_2.

In *sulphur dioxide* (SO_2)

Sulphur and oxygen combine in the ratio of 32 : 32 or 1 : 1 ...(*ii*)

The two ratios (*i*) and (*ii*) are related to each other as

$$\frac{2}{1} : \frac{1}{1} \text{ or } 2 : 1$$

which are simple multiple of each other.

However, sulphur and oxygen also react to form sulphur trioxide (SO_3) which is also in accordance with the law.

In *sulphur trioxide* (SO_3)

Sulphur and oxygen combine in the weight ratio of 32 : 48 or 2 : 3 ...(*iii*)

The two ratios (*i*) and (*iii*) are also related to each other as

$$\frac{2}{1} : \frac{2}{3} \text{ or } 3 : 1$$

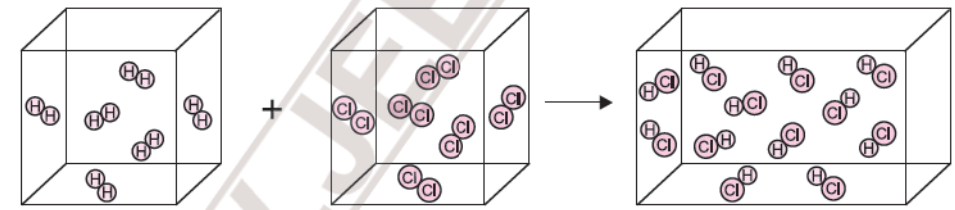
which are simple multiple of each other.

5. Gay Lussac's Law of Combining Volumes

Gay Lussac performed a number of experiments on reactions involving gases and found that some regularity exists between the volumes of the gaseous reactants and products. In 1808, he put forward a generalisation known as **Gay Lussac's law of combining volumes.** It states that

when gases react together or produced in a chemical reaction, they do so in a simple ratio by volume to one another and to the volumes of the products (if these are also gases) provided all gases are at the same temperature and pressure.

This law may be illustrated by the following examples :



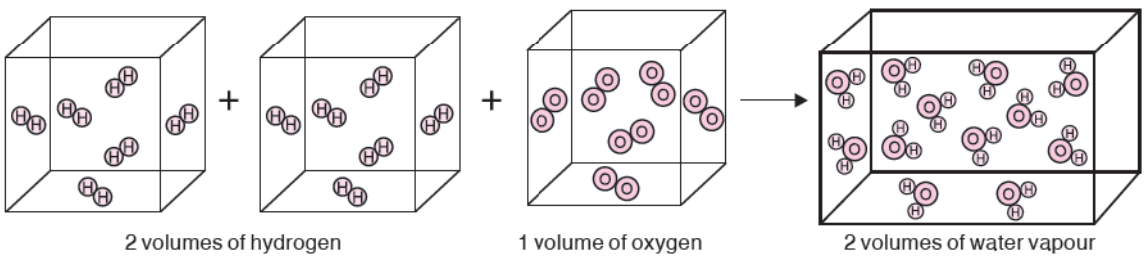
It has been experimentally found that 1 volume of hydrogen reacts with 1 volume of chlorine to give 2 volumes of hydrogen chloride as :

Thus, the volume ratio of hydrogen : chlorine : hydrogen chloride is 1 : 1 : 2. This is a simple whole number ratio and is also in agreement with their molar ratios when they are involved in the reaction.

$$\underset{\text{1 volume}}{H_2(g)} + \underset{\text{1 volume}}{Cl_2(g)} \longrightarrow \underset{\text{2 volumes}}{2HCl(g)}$$

For example, 100 mL of hydrogen combine with 100 mL of chlorine to give 200 mL of hydrogen chloride.

Similarly, we observe that 2 volumes of hydrogen combine with 1 volume of oxygen to give 2 volumes of water vapour as



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Thus, the volumes of hydrogen and oxygen which combine to form water is in the ratio : 2 : 1 : 2.

$$\underset{\text{2 volumes}}{2H_2(g)} + \underset{\text{1 volume}}{O_2(g)} \longrightarrow \underset{\text{2 volumes.}}{2H_2O(g)}$$

Similarly, it has been found that one volume of nitrogen combines with three volumes of hydrogen to give two volumes of ammonia gas.

$$\underset{\text{1 volume}}{N_2(g)} + \underset{\text{3 volumes}}{3H_2(g)} \longrightarrow \underset{\text{2 volumes}}{2NH_3}$$

SOLVED EXAMPLES

Example 18.

If 6.3 g of $NaHCO_3$ are added to 15.0 g of CH_3COOH solution, the residue is found to weigh 18.0 g. What is the mass of CO_2 released in the reaction ?

Solution:

$$\underset{\text{6.3 g}}{NaHCO_3} + \underset{\text{15.0 g}}{CH_3COOH} \longrightarrow \underbrace{CH_3COONa + H_2O}_{\substack{\text{Residue}\\ \text{18.0 g}}} + \underset{x\,g}{CO_2}$$

Sum of the mass of reactants = Mass of $NaHCO_3$ + Mass of CH_3COOH
= 6.3 + 15.0 = 21.3 g

Sum of the mass of products = Mass of residue + Mass of CO_2
(18.0 + x) g
(where x is mass of CO_2 released)

According to law of conservation of mass

Mass of reactants = Mass of products

$21.3 = 18.0 + x$

or $x = 21.3 - 18.0 = 3.3$ g

$\therefore$ Mass of CO_2 released = **3.3 g**

Example 19.

Carbon and oxygen are known to form two compounds. The carbon content in one of these compounds is 42.9% while in the other, it is 27.3%. Show that the data are in the agreement with the law of multiple proportions. ***N.C.E.R.T.***

Solution: *In the first compound,*

Mass of carbon = 42.9 g

Mass of oxygen = 100 – 42.9 = 57.1 g

In the second compound,

Mass of carbon = 27.3 g

Mass of oxygen = 100 – 27.3 = 72.7 g

In the first compound.

Mass of carbon combining with 57.1 g of oxygen = 42.9 g

Mass of carbon combining with 1.0 g of

$$\text{oxygen} = \frac{42.9\text{ g}}{57.1} = 0.75\text{ g}$$

In the second compound,

Mass of carbon combining with 72.7 g of

oxygen = 27.3 g

Mass of carbon combining with 1.0 g of

$$\text{oxygen} = \frac{27.3}{72.7} = 0.375\text{ g}$$

The ratio of mass of carbon combining with fixed mass of oxygen (*i.e.*, 1 g) is

0.75 : 0.375 or **2 : 1.**

This is a simple ratio and therefore, illustrates the **law of multiple proportions**.

Example 20.

2.0 g of a metal burnt in oxygen gave 3.2 g of its oxide. 1.42 g of the same metal heated in steam gave 2.27 g of its oxide. Which law is shown by this data?

Solution: In the first compound,

3.2 g of metal oxide contained 2.0 g of metal

100 g of metal oxide contained metal

$$= \frac{2.0}{3.2} \times 100 = 62.5\text{ g}$$

$\therefore$ % Metal in first compound = 62.5%

In the second compound,

2.27 g of metal oxide contained metal = 1.42 g

100 g of metal oxide contained metal

$$= \frac{1.42}{2.27} \times 100 = 62.55\text{ g}$$

$\therefore$% Metal in second compound = 62.55%

Thus, the percentage of metal in metal oxide obtained from two experiments is nearly same. Hence, the above data illustrate the law of constant composition.

Example 21.

Phosphorus and chlorine form two compounds. The first compound contains 22.54% by mass of phosphorus and 77.46% by mass of chlorine. In the second compound the percentages are 14.88 for phosphorus and 85.12 for chlorine. Show that these data are consistent with the law of multiple proportions.

Solution: *In the first compound,*

Percentage of phosphorus = 22.54

Percentage of chlorine = 77.46

Thus, 22.54 g of phosphorus combines with 77.46 g of chlorine.

In the second compound,

Percentage of phosphorus = 14.88

Percentage of chlorine = 85.12

Thus, 14.88 g of phosphorus combine with 85.12 g of chlorine.

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Let us fix the mass of phosphorus as 1 g and find the different masses of chlorine which combine with 1 g of phosphorus in two compounds.

In the first compound,

Mass of chlorine which combines with 22.54 g of phosphorus = 77.46 g

The mass of chlorine which combines with 1 g of phosphorus = $\frac{77.46}{22.54}$ = 3.44 g

In the second compound,

Mass of chlorine which combines with 14.88 g of phosphorus = 85.12 g

Mass of chlorine which combines with 1 g of phosphorus

$$= \frac{85.12}{14.88} = 5.72$$

The ratio of the masses of chlorine which combines with the fixed mass of phosphorus (1 g) in the two compounds is

3.44 : 5.72

1 : 1.66 or 3 : 5 (approximately)

This is a simple whole number ratio. Therefore, the data is in agreement with the **law of multiple proportions.**

❑ Example 22.

Three oxides of lead on analysis were found to contain lead as under :

(i) 3.45 g of yellow oxide contains 3.21 g of lead.

(ii) 1.195 g of brown oxide contains 1.035 g of lead.

(iii) 1.77 g of red oxide contains 1.61 g of lead.

Show that these data illustrate law of multiple proportions.

Solution: The amounts of lead and oxygen in three oxides are :

(*i*) Yellow oxide : Mass of lead = 3.21 g

Mass of oxygen = 3.45 – 3.21 = 0.24 g

(*ii*) Brown oxide : Mass of lead = 1.035 g

Mass of oxygen = 1.195 – 1.035 = 0.160 g

(*iii*) Red oxide : Mass of lead = 1.61 g

Mass of oxygen = 1.77 – 1.61 = 0.16 g

Let us fix the mass of lead as 1 g and calculate the different weights of oxygen which combine with 1 g of lead in these oxides.

(*i*) *Yellow oxide*

Mass of oxygen which combines with 3.21 g of lead = 0.24 g

Mass of oxygen which combines with 1 g of lead

$$= \frac{0.24}{3.21} = 0.075 \text{ g}$$

(*ii*) *Brown oxide*

Mass of oxygen which combines with 1.035 g of lead = 0.160 g

Mass of oxygen which combines with 1 g of lead

$$= \frac{0.160}{1.035} = 0.15 \text{ g}$$

(*iii*) *Red oxide*

Mass of oxygen which combines with 1.61 g of lead = 0.16 g

Mass of oxygen which combines with 1 g of lead

$$= \frac{0.16}{1.61} = 0.10 \text{ g}$$

The ratio of different masses of oxygen which combine with same mass of lead (1 g) in these oxides is :

0.075 : 0.15 : 0.10

3 : 6 : 4

This is a simple ratio.

Hence, the data illustrate the **law of multiple proportions.**

❑ Example 23.

Two oxides of a metal contain 27.6% and 30% of oxygen respectively. If the formula of the first compound is M_3O_4, find the formula of the second compound.

Solution:

First oxide	*Second oxide*
Oxygen = 27.6%	Oxygen = 30%
Metal = 72.4%	Metal = 70%

Formula of first oxide = M_3O_4

Suppose the atomic weight of metal = x

Percentage of metal in the compound M_3O_4

$$= \frac{3x}{3x + 64} \times 100$$

$$\therefore \quad \frac{3x}{3x + 64} \times 100 = 72.4$$

or $300\,x = 217.2\,x + 4633.6$

or $82.8\,x = 4633.6$ or $x = 56$

Now in the second oxide, metal and oxygen are 70% and 30%. Therefore, their atomic ratio will be

M : O

$\frac{70}{56} : \frac{30}{16}$

1.25 : 1.875

or 1 : 1.5

or 2 : 3

Therefore, formula of the compound = $\mathbf{M_2O_3}$.

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❑ **Example 24.**

Hydrogen sulphide (H_2S) contains 94.11% sulphur, water (H_2O) contains 11.11% hydrogen and sulphur dioxide (SO_2) contain 50% oxygen. Show that the results are in agreement with law of reciprocal proportions.

Solution:

In water (H_2O)

Mass of hydrogen = 11.11 g

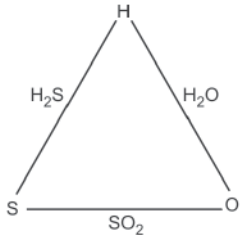
Mass of oxygen = 100 – 11.11 g

= 88.89 g

In sulphur dioxide (SO_2)

Mass of sulphur = 50 g

Mass of oxygen = 100 – 50 g = 50 g



Let us fix the mass of oxygen as 1 g.

Now in H_2O,

88.89 g of oxygen combine with hydrogen = 11.11

$$1 \text{ g of oxygen combines with hydrogen} = \frac{11.11}{88.89} \times 1$$

$$= 0.125 \text{ g}$$

In SO_2,

50 g of oxygen combine with sulphur = 50 g

$$1 \text{ g of oxygen combines with sulphur} = \frac{50}{50} \times 1 = 1 \text{ g}$$

Thus, the ratio of the masses of hydrogen and sulphur which combine with the fixed mass of oxygen (1 g) is

0.125 : 1 or 1 : 8 ...(*i*)

In hydrogen sulphide (H_2S)

Mass of sulphur = 94.11 g

Mass of hydrogen = 100 – 94.11 = 5.89 g

Therefore, the ratio by mass of hydrogen and sulphur in hydrogen sulphide is

5.89 : 94.11 or 1 : 16 ...(*ii*)

The ratios (*i*) and (*ii*) are

$$\frac{1}{8} : \frac{1}{16} \text{ or } 2 : 1$$

which is simple whole number.

Hence, the law of reciprocal proportions is verified.

❑ **Example 25.**

Water contains 88.90% oxygen and 11.10% of hydrogen, ammonia contains 82.35% of nitrogen and 17.65% of hydrogen and dinitrogen trioxide contains 63.15% oxygen and 36.85% of nitrogen. Show that these data illustrate law of reciprocal proportions.

Solution:

In water (H_2O)

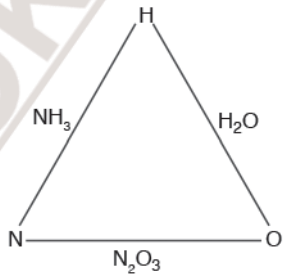
Mass of hydrogen = 11.10 g

Mass of oxygen = 88.90 g

In ammonia (NH_3)

Mass of hydrogen = 17.65 g

Mass of nitrogen = 82.35 g



Let us fix the mass of hydrogen as 1 g.

Now in H_2O,

11.10 g of hydrogen combine with oxygen = 88.90 g

$$1 \text{ g of hydrogen combines with oxygen} = \frac{88.90}{11.9}$$

$$= 8.01 \text{ g}$$

In NH_3,

17.65 g of hydrogen combine with nitrogen = 82.35 g

$$1 \text{ g of hydrogen combines with nitrogen} = \frac{82.35}{17.65}$$

$$= 4.67 \text{ g}$$

Thus, the ratio of nitrogen and oxygen which combine with the fixed mass of hydrogen (1 g) is

4.67 : 8.01 or 1 : 1.172 ...(*i*)

In dinitrogen trioxide

Mass of nitrogen = 36.85 g

Mass of oxygen = 63.15 g

Therefore, the ratio by mass of nitrogen and oxygen in dinitrogen trioxide is

36.85 : 63.15 or 1 : 1.172 ...(*ii*)

Thus, the two ratios are the same. Hence, it illustrates the law of reciprocal proportions.

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Practice Problems

21. When 4.2 g of $NaHCO_3$ is added to a solution of CH_3COOH (acetic acid) weighing 10.0 g, it is observed that 2.2 g of CO_2 is released to the atmosphere. The residue left is found to weigh 12.0 g. Show that these observations are in agreement with the law of conservation of mass.

Hint : Mass of reactants = 14.2 g : Mass of products = 14.2 g

22. Hydrogen peroxide and water contain 5.93% and 11.2% of hydrogen respectively. Show that the data illustrates law of multiple proportions.

Hint : The ratio of weights of oxygen combining with 1 g of hydrogen is 2 : 1.

23. Elements A and B combine to form two different compounds as :

0.3 g of A + 0.4 g of B $\longrightarrow$ 0.7 g of compound X

18 g of A + 48 g of B $\longrightarrow$ 66 g of compound Y.

Show that the data illustrates the law of multiple proportions.

24. Carbon combines with hydrogen to form compounds having the following compositions :

Compound	Carbon (%)	Hydrogen (%)
A	75	25
B	85.7	14.3
C	92.3	7.7

Show that the data illustrate the law of multiple proportions.

Hint : Ratio between weights of H which combine with fixed weight of C is 4 : 2 : 1.

25. 1.375 g CuO was reduced by hydrogen and 1.098 g Cu was obtained. In another experiment, 1.178 g of Cu was dissolved in nitric acid and the resulting copper nitrate was converted into CuO by ignition. The weight of CuO formed was 1.476 g. Show that these results prove the law of constant composition.

26. Illustrate the law of definite proportions from the following data :

(*i*) 0.32 g of sulphur on burning in air produced 224 ml of SO_2 at N.T.P.

(*ii*) A metal sulphite reacts with a mineral acid to give SO_2 gas which contains 50% of sulphur and 50% of oxygen.

27. Copper sulphate crystals contain 25.45% Cu and 36.07% H_2O. If the law of constant proportions is true then calculate the weight of Cu required to obtain 40 g of crystalline copper sulphate.

Ans. 10.18 g

28. Copper sulphide contains 66.5% Cu, copper oxide contains 79.9% Cu and sulphur trioxide contains 40% S. Show that the data illustrates the law of reciprocal proportions.

29. Two oxides of a certain metal were separately heated in a current of hydrogen until constant weights were obtained. The water produced in each case was carefully collected and weighed. It was observed that 1 g of each oxide gave 0.1254 g and 0.2263 g of water respectively. Show that the data illustrate the law of multiple proportion.

Hints & Solutions on page 79

DALTON ATOMIC THEORY

To provide theoretical justification to the laws of chemical combination, John Dalton postulated a simple theory of matter. The **basic postulates** of the theory are given below :

(*i*) *Matter is made up of extremely small indivisible and indestructible ultimate particles called atoms.*

(*ii*) *Atoms of the same element are identical in all respects i.e. in shape, size, mass and chemical properties.*

(*iii*) *Atoms of different elements are different in all respects and have different masses and chemical properties.*

(*iv*) *Atom is the smallest unit that takes part in chemical combinations.*

(*v*) *Atoms of two or more elements combine in a fixed ratio to form compound atoms (now a days called molecules).*

(*vi*) *Atoms can neither be created nor destroyed during any physical or chemical change.*

(*vii*) *Chemical reactions involve only combination, separation or rearrangement of atoms.*

Limitations of Dalton's Atomic Theory

Dalton' s atomic theory gave a powerful initiative to scientists in the beginning of the 19th century. The main achievement of the theory was that one could derive the laws of chemical combination from it. It held the field for a century. But as a result of discoveries in the beginning of 20th century by Sir J. J. Thomson, Rutherford, Neils Bohr and others, the atomic theory was reviewed and modified. The main drawbacks of Dalton's atomic theory are :

(*i*) It could explain the laws of chemical combination by mass but failed to explain the law of gaseous volumes.

(*ii*) It could not explain why atoms of different elements have different masses, sizes, valencies, etc.

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(*iii*) It could not explain how and why atoms of different elements combine with each other to form compound atoms or molecules.

(*iv*) It failed to explain the nature of forces that bind together atoms in a molecule.

(*v*) It gave no satisfactory explanation between the ultimate particle of an element and that of a compound.

Modern Atomic Theory

The main modifications made in the Dalton's atomic theory as a result of new discoveries about atom are :

1. Atom is no longer considered to be indivisible. It has been found that an atom has a complex structure and is made up of subatomic particles such as electrons, protons and neutrons.

2. Atoms of same elements may not be similar in all respects. Atoms of same element may possess different relative masses. For example, there are two different types of atoms of chlorine with atomic masses 35 a.m.u. and 37 a.m.u. respectively. Such atoms of the same element which possess different atomic masses are called **isotopes.**

3. Atoms of different elements may have similar one or more properties. There are certain atoms of different elements which possess same relative masses. For example, atomic mass of calcium and argon is same (40 a.m.u.) but their chemical properties are entirely different. Such atoms of different elements which possess same mass are called **isobars.**

4. Atom is the smallest unit which takes part in chemical reactions. Though an atom is composed of subatomic particles yet it is the smallest particle which takes part in chemical reactions.

5. The ratio in which the different atoms combine may be fixed and integral but may not always be simple. For example, in sugar molecule ($C_{12}H_{22}O_{11}$), the ratio of C, H and O atoms is 12 : 22 : 11, which is not simple.

6. Atom of one element may be changed into atoms of other element. For example, atoms of nitrogen can be changed into oxygen atoms by interaction with α-rays. Similarly, uranium ($^{235}_{92}U$) can be converted into plutonium ($^{239}_{94}Pu$) through interaction with neutrons. This process is called **transmutation.** Thus, atom is no longer indestructible.

7. The mass of atom can be changed into energy. According to Einstein's equation, $E = mc^2$ (E = energy, m = mass and c = velocity of light), mass and energy are interconvertible. Thus, **atom is no longer indestructible**. However, during chemical reactions, atom remains unchanged.

AVOGADRO'S HYPOTHESIS

While trying to correlate Gay Lussac's law of gaseous volumes and Dalton's atomic theory, Berzelius, the Swedish scientist, put forward a generalisation, in 1811 known as *Berzelius hypothesis.* According to **Berzelius hypothesis :**

equal volumes of all gases contain equal number of atoms under similar conditions of temperature and pressure.

However, when the Berzelius hypothesis was applied to some chemical reactions it was observed that even a fraction of atoms was involved in some cases. The idea of fraction of atoms is against the concept of Dalton's atomic theory :

For example, consider the formation of hydrochloric acid gas (HCl). It has been observed experimentally that one volume of hydrogen combines with one volume of chlorine to produce two volumes of hydrochloric acid gas. This may be expressed as :

Hydrogen	+	Chlorine	⟶	Hydrochloric acid gas
1 vol		1 vol		2 vols

According to Berzelius hypothesis, equal volumes will contain equal number of atoms. Let one volume contains n atoms :

Hydrogen	+	Chlorine	⟶	Hydrochloric acid gas
or n atoms		n atoms		$2n$ compound atoms
or 1 atom		1 atom		2 compound atoms
½ atom		½ atom		1 compound atom

This means that one compound atom of hydrochloric acid gas is formed by the combination of ½ atom of hydrogen and ½ atom of chlorine. This means that fraction of atoms take part in chemical combination and therefore, atoms may undergo division during chemical reactions. But this idea of fraction of atoms is against the concept of Dalton's atomic theory according to which atom is the smallest unit of an element which takes part in chemical reactions.

To solve this problem of conflict between the Dalton's atomic theory and Berzelius hypothesis, **Avogadro** suggested that matter consists of two kinds of ultimate particles. These are *atoms* and *molecules.* According to him,

the smallest particle of an element which may or may not have independent existence and takes part in a chemical reactions *is called* ***an atom.***

The smallest particle of a substance (element or compound) capable of independent existence *is called* ***a molecule.***

Thus, the smallest particles of gases which can have independent existence are molecules and not the atoms and therefore, volume of gases should be related to number of molecules and not number of atoms. He could explain the results by considering the molecules to be **polyatomic.** He put forward a hypothesis known as **Avogadro's law.** It may be stated as :

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under similar conditions of temperature and pressure, equal volumes of all gases contain equal number of molecules.

Mathematically, we can say

$$V \propto N$$

where N is the number of molecules.

For example, if we enclose equal volumes of three gases hydrogen (H_2), oxygen (O_2) and chlorine (Cl_2) in different flasks of the same capacity under similar conditions of temperature and pressure, we find that all the flasks have the same number of molecules. However, these molecules may differ in size and mass.

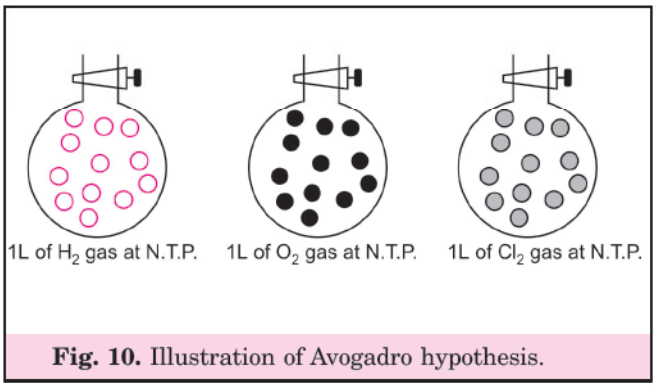

Fig. 10. Illustration of Avogadro hypothesis.

Gay-Lussac and Avogadro's laws can be illustrated as follows :

	$2H_2(g)$	+	$O_2(g)$	⟶	$2H_2O\ (g)$
Gay-Lussac's law	2 vol		1 vol		2 vol
Avogadro's law	$2n$ molecules		n molecules		$2n$ molecules
	2 molecules		1 molecule		2 molecules

	$N_2(g)$	+	$3H_2(g)$	⟶	$2NH_3\ (g)$
Gay-Lussac's law	1 vol		3 vol		2 vol
Avogadro's law	n molecules		$3n$ molecules		$2n$ molecules
	1 molecule		3 molecules		2 molecules

The Avogadro hypothesis can be successfully applied to different chemical reactions.

Formation of Hydrochloric acid gas

Consider the formation of hydrochloric acid gas. It is observed that 1 volume of hydrogen combines with 1 volume of chlorine to give 2 volumes of hydrogen chloride (all volumes under same conditions).

Hydrogen	+	Chlorine	⟶	Hydrogen chloride
1 vol		1 vol		2 vols

Applying Avogadro's hypothesis assuming that 1 volume contains n molecules, it follows that

Hydrogen	+	Chlorine	⟶	Hydrogen chloride
n molecules		n molecules		$2n$ molecules

Dividing throughout by $2n$, we get

$\frac{1}{2}$molecule $\frac{1}{2}$molecule 1 molecule

This means that 1 molecule of hydrogen chloride contain ½ molecule of hydrogen and ½ molecule of chlorine.

Now ½ molecule of hydrogen can exist because one molecule of hydrogen contains 2 atoms of hydrogen and ½ molecule of hydrogen means one atom of hydrogen. Similarly, ½ molecule of chlorine contains an atom of chlorine because chlorine is also a diatomic molecule. Thus, one molecule of hydrogen chloride is formed from one atom of hydrogen and one atom of chlorine. *This is in agreement with Dalton's atomic theory.*

Applications of Avogadro's Law

1. Deduction of Atomicity of Elementary Gases

The number of atoms present in its one molecule of the substance is called its **atomicity.** Avogadro's law helps in determining the atomicity of elementary gases such as hydrogen, oxygen, chlorine, etc. For example,

Atomicity of oxygen. The atomicity of oxygen can be calculated by considering the reaction between hydrogen and oxygen to form water vapour. It has been experimentally found that 2 volumes of hydrogen react with 1 volume of oxygen to form 2 volumes of water vapour.

Hydrogen	+	Oxygen	⟶	Water vaopur
2 volumes		1 volume		2 volumes

Applying Avogardro's hypothesis

2 n molecules	n molecules	$2n$ molecules
2 molecules	1 molecule	2 molecules
1 molecule	$\frac{1}{2}$molecule	1 molecule

Thus, one molecule of water contains one molecule of hydrogen (2 atoms) and ½ molecule of oxygen. The molecular mass of water has been found to be 18 a.m.u. Since one molecule of hydrogen contains two atoms of hydrogen, therefore, weight of oxygen is one molecule of water is 18 – 2 = 16 a.m.u. This corresponds to the weight of one atom of oxygen. Thus, one atom is present in half molecule of oxygen. Therefore,

$\frac{1}{2}$ molecule of oxygen = 1 atom

or 1 molecule of oxygen = 2 atoms

Thus, **atomicity of oxygen is 2.**

2. Determination of relationship between vapour density and molar mass of a gas

The vapour density of a gas is *the ratio between the mass of a certain volume of the gas to the mass of the same volume of hydrogen gas under similar*

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conditions of temperature and pressure. Thus,

Vapour density (V.D.) of a gas

$$= \frac{\text{Mass of certain volume of gas}}{\text{Mass of same volume of hydrogen}}$$

(similar conditions)

According to Avogadro's hypothesis, equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules. Let the given volume of the gas and hydrogen contain n molecules at S.T.P. conditions.

Vapour density

$$= \frac{\text{Mass of } n \text{ molecules of gas}}{\text{Mass of } n \text{ molecules of hydrogen}}$$

$$= \frac{\text{Mass of 1 molecule of gas}}{\text{Mass of 1 molecule of hydrogen}}$$

Since 1 molecule of hydrogen contains 2 atoms of hydrogen,

$$\text{Vapour density} = \frac{\text{Mass of 1 molecule of gas}}{\text{Mass of 2 atoms of hydrogen}}$$

But the ratio of the mass of one molecule of gas to the mass of an atom of hydrogen is called molar mass (discussed later).

$$\therefore \text{ Vapour density } = \frac{\text{Molar mass}}{2}$$

or **Molar mass = 2 × Vapour density**

Vapour density is also called *relative density* of the gas.

3. Determination of relationship between mass and volume of gas.

As discussed above,

$$\text{Molar mass} = 2 \times \text{Vapour density}$$

$$= 2 \times \frac{\text{Mass of certain volume of gas at S.T.P.}}{\text{Mass of same volume of hydrogen at S.T.P.}}$$

$$= 2 \times \frac{\text{Mass of 1L of gas at S.T.P.}}{\text{Mass of 1L of hydrogen at S.T.P.}}$$

But mass of 1L of hydrogen gas is 0.089 g

$$\therefore \text{ Molar mass} = 2 \times \frac{\text{Mass of 1L of gas at S.T.P.}}{0.089}$$

$$= \frac{2}{0.089} \times \text{Mass of 1L of gas at S.T.P.}$$

$$= 22.4 \times \text{Mass of 1L of gas at S.T.P.}$$

$$= \text{Mass of 22.4L of gas at S.T.P.}$$

Thus, 22.4 L of any gas at S.T.P. weigh equal to molar mass of gas expressed in grams. This is also called **Gram Molecular Volume (G.M.V.).**

add on Conceptual Questions 1

CONCEPTUAL QA

Q.1. How many significant figures are there in each of the following numbers :
(*i*) 1.00×10^6 (*ii*) 0.00010 (*iii*) π

Ans. (*i*) Three (*ii*) Two (*iii*) an infinite number.

Q.2. Convert 22.4 L in cubic metres.

Ans.
$$22.4 \text{ L} \times \left(\frac{10^3 \text{cm}^3}{\text{L}}\right) = 22.4 \times 10^3 \text{cm}^3$$

$$= 22.4 \times 10^3 \text{cm}^3 \times \left(\frac{10^{-6} \text{m}^3}{\text{cm}^3}\right)$$

$$= 22.4 \times 10^{-3} \text{ m}^3$$

Q.3. What physical quantities are represented by the following units and what are their common names ?
(*i*) kg m^2 s^{-2} (*ii*) kg m s^{-2} (*iii*) dm^3

Ans. (*i*) Energy, Joule (*ii*) Force, Newton (*iii*) Volume, Litre.

Q.4. The longest visible rays, at the end of the visible spectrum are 7.8×10^{-7} m in length. Express this length in (*i*) micrometers and (*ii*) nanometers.

Ans. (*i*)
$$1 \text{ m} = 10^6 \text{ μm}$$

$$\text{Unit factor} = \frac{10^6 \text{μm}}{1 \text{m}}$$

$$\therefore \quad 7.8 \times 10^{-7} \text{ m} = 7.8 \times 10^{-7} \text{m} \times \frac{10^6 \text{μm}}{1 \text{m}} = 0.78 \text{ μm}$$

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(*ii*) $1\text{m} = 10^9\text{ nm}$

$$\text{Unit factor} = \frac{10^9\text{ nm}}{1\text{m}}$$

$$\therefore \quad 7.8 \times 10^{-7}\text{ m} = 7.8 \times 10^{-7}\text{ m} \times \frac{10^9\text{ nm}}{1\text{m}} = 780\text{ nm.}$$

Q.5. Which of the following mixture are homogeneous ?

(*a*) tap water (*b*) air (*c*) soil (*d*) smoke (*e*) cloud

Ans. Tap water, air, cloud.

Q.6. Is the molar volume of CO_2 same or different from CO ?

Ans. Same.

Q.7. At what temperature have the Celsius and Fahrenheit reading the same numerical value ?

Ans.
$$^\circ\text{C} = \frac{5}{9}(\text{F} - 32)$$

$$x = \frac{5}{9}(x - 32)$$

$$4x = -160 \qquad \therefore x = -40$$

$\therefore -40^\circ\text{C}, \quad -40^\circ\text{F}.$

Q.8. What is the difference between 0.006 and 6.00×10^{-3} g ?

Ans. 0.006 g contains one significant digit while 6.00×10^{-3} g contains 3 significant digits.

Q.9. Calssify the following substances into elements, compounds and mixtures :

(*i*) Milk (*ii*) 22 carat gold (*iii*) Iodized table salt (*iv*) Diamond (*v*) Smoke (*vi*) Steel (*vii*) Brass (*viii*) Dry ice (*ix*) Mercury (*x*) Air (*xi*) Aerated drinks (*xii*) Glucose (*xiii*) Petrol (*xiv*) Glass (*xv*) Wood

Ans. Elements : (*iv*), (*ix*)

Compounds : (*viii*), (*xii*)

Mixtures : (*i*), (*ii*), (*iii*), (*v*), (*vi*), (*vii*), (*x*), (*xiii*), (*xiv*), (*xv*)

N.C.E.R.T.

Q.10. Given that density of water is 1 g mL^{-1}. What is the density in SI units?

Ans. $1\text{ g mL}^{-1} = 1\text{ g cm}^{-3} = 1\,\cancel{g} \times \left(\frac{1\text{ kg}}{1000\,\cancel{g}}\right) \times \frac{1}{\cancel{\text{cm}^3}} \times \left(\frac{100\,\cancel{\text{cm}}}{1\text{ m}}\right)^3$ **= 1000 kg m^{-3}.**

Q.11. Is the law of constant composition true for all types of compounds? Explain why or why not?

Ans. Law of constant composition is not true for all types of compounds. It is true only for the compounds obtained from one isotope. For example, carbon exists in two common isotopes, ^{12}C and ^{14}C. When CO_2 is formed from ^{12}C, the ratio of masses is 12 : 32 or 3 : 8, but when it is formed from ^{14}C, the ratio will be 14 : 32 or 7 : 16, which is not same as in first case.

Q.12. Which postulate of the Dalton's atomic theory was modified after the discovery of isotopes ?

Ans. According to postulates of the Dalton's atomic theory, atoms of same element are identical in all respects *i.e.*, in shape, size, mass and chemical properties. However, after the discovery of isotopes, it was modified as : atoms of same element may not be similar in all respects. For example, there are two types of atoms of chlorine with atomic masses 35 amu and 37 amu respectively (called isotopes).

ATOMS AND MOLECULES

Atom

Atom is the ultimate particle of an element. To understand this, consider a piece of an element, say gold. If we break this into smaller and smaller pieces, it will become so small that we will not be able to see it without a microscope. If we keep on breaking this particle, we will ultimately reach a stage when this particle cannot be further broken. This ultimate particle of an element is called an **atom.** Thus,

the smallest particle of an element which may or may not have independent existence is called an **atom**.

The atoms of certain elements, such as hydrogen, oxygen, nitrogen, etc. are not capable of independent existence whereas atoms of helium, neon, argon, etc., are capable of independent existence.

All elements are composed of atoms. There are about 118 elements known and therefore, there are 118 different types of atoms.

Molecule

Just as the ultimate particle of an element is **atom,** the ultimate particle of a chemical compound is called a **molecule.** When two or more atoms of different elements combine, the molecule of a comound is formed. For example,

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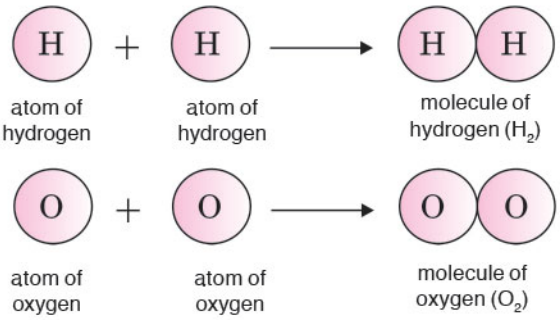


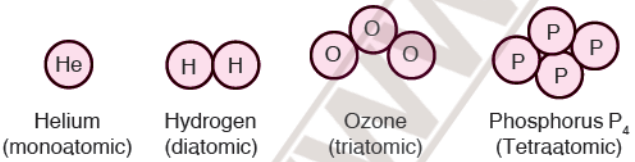
The molecules are made up of atoms of the same or different elements and are capable of independent existence. Thus,

the smallest particle of a substance (element or compound) which is capable of independent existence *is called a* **molecule.**

Thus, a molecule contains two or more atoms. The properties of a substance are due to the properties of its molecules. Molecules can be classified into two types :

(*i*) **Homoatomic molecules.**

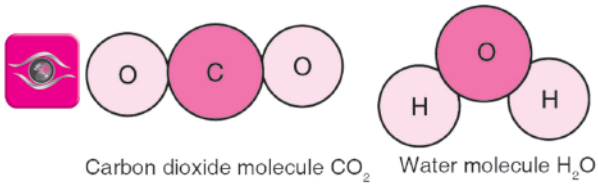
These molecules are made up of the atoms of the same element. Most of the elementary gases consist of homoatomic molecules. For example, hydrogen gas consists of two atoms of hydrogen (H_2). Similarly, chlorine gas consists of two atoms of chlorine (Cl_2). Similarly, nitrogen and oxygen gases are N_2 and O_2, respectively. These molecules may be further classified as *monoatomic, diatomic, triatomic,* or *polyatomic* molecules according as they contain one, two, three or more than three atoms respectively. The number of atoms in a molecule of an element is called **atomicity.** For example, He, Ne (monoatomic), O_2, N_2, H_2 (diatomic), O_3 (triatomic), P_4 (tetraatomic), S_8 (polyatomic), etc.

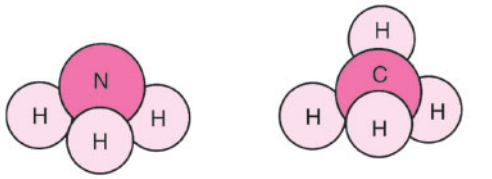


(*ii*) **Heteroatomic molecules.**

These molecules are made up of atoms of different elements. They are also classified as di, tri, tetra...etc. depending upon the number of atoms present. For example H_2O, HCl, CO_2, NH_3, CH_4, PCl_5 are heteroatomic molecules.

The molecules of some common compounds are shown below :





ATOMIC AND MOLECULAR MASSES

Atomic Mass

An atom of an element is so small particle that its mass cannot be determined even with the help of most sensitive balance. For example, by an indirect method, the absolute mass of hydrogen atom has been found to be 1.6736×10^{-24} g. Such extremely small numbers are very inconvenient for calculations. The difficulty was overcome by expressing *atomic masses, as* ***relative masses****. i.e., with respect to the mass of an atom of a standard substance.*

Earlier the chemists selected **hydrogen** atom as the standard substance because it is the lightest of all known atoms. The atomic mass of hydrogen was taken as one. Thus, the **atomic mass** of an element *is the number of times an atom of that element is heavier than an atom of hydrogen*. The relative atomic masses were referred to as the **atomic weights.** For example, it has been found that an atom of oxygen is 16 times heavier than an atom of hydrogen. Thus, the atomic mass of oxygen relative to hydrogen is 16. Later on, oxygen was fixed as the standard because it is more reactive than hydrogen and forms a large number of compounds.

In 1961, the International Union of Chemists selected a new unit for expressing the atomic masses. They accepted the isotope of carbon (^{12}C) with mass number 12 as the standard for comparing the atomic and molecular masses of elements and compounds. Carbon-12 is the stablest isotope of carbon and can be represented as ^{12}C.

Thus, **atomic mass of an element** is defined as

the average relative mass of an atom of an element as compared to the mass of an atom of carbon (^{12}C) taken as 12.

In other words, atomic mass is a number which expresses *as to how many times an atom of the element is heavier than 1 / 12th of the mass of carbon atom* (^{12}C).

Therefore,

$$\text{Atomic mass} = \frac{\text{Mass of an atom}}{\frac{1}{12}\text{ mass of a carbon atom } (^{12}C)}$$

This scale of relative masses of atoms is called **atomic mass unit scale** and is abbreviated as a.m.u. However, the new symbol used is 'u' (known as unified mass) in place of a.m.u. In this system, **^{12}C is assigned a mass of exactly 12 atomic mass unit** and masses

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of all other atoms are given relative to this standard. Hence, **one atomic mass unit** is defined as

the quantity of mass equal to 1/12th of the mass of an atom of carbon (^{12}C).

Mass of 1amu has been calculated to be

1 amu = 1.66056×10^{-24} g

Mass of an atom of hydrogen = 1.6736×10^{-24} g

Thus, in terms of amu, the mass of hydrogen atom

$$= \frac{1.6736 \times 10^{-24}\ g}{1.66056 \times 10^{-24}\ g} = 1.008 \text{ amu}$$

Thus, the atomic mass of hydrogen is 1.008 u. Similarly, the mass of oxygen – 16 (^{16}O) atom is 15.995 u or 16 u; of nitrogen is 14 u and of sulphur is 32 u. This means that an atom of hydrogen is 1.008 times heavier than 1/12th of the mass of carbon atom (^{12}C); an atom of oxygen is 16 times heavier than $^1/_{12}$th of the mass of carbon atom (^{12}C) and so on.

The atomic masses of some common elements are given in Table 7. It may be noted that only the approximate values of atomic masses which are normally used in the chemical calculations, are given. For example, atomic mass of hydrogen is 1.008 g but it is taken as 1.

Nowadays atomic masses of the elements have been determined accurately using an instrument called **mass spectrometer.**

Table 7. Atomic mass of a few common elements referred to ^{12}C = 12.0

Element	Symbol	Atomic mass
Aluminium	Al	27.0
Antimony	Sb	121.8
Arsenic	As	74.9
Argon	Ar	18
Beryllium	Be	9.01
Bismuth	Bi	209
Boron	B	10.8
Bromine	Br	79.9
Calcium	Ca	40.1
Carbon	C	12.0
Chlorine	Cl	35.5
Copper	Cu	63.5
Fluorine	F	19.0
Helium	He	4.0
Hydrogen	H	1.0
Iodine	I	126.9
Irone	Fe	55.8
Lead	Pb	207.2
Lithium	Li	6.94
Manganese	Mn	54.9
Magnesium	Mg	24.3
Mercury	Hg	200.6
Neon	Ne	20.2
Nickel	Ni	58.7
Nitrogen	N	14.0
Oxygen	O	16.0
Phosphorus	P	31.0
Potassium	K	39.0
Silicon	Si	28.1
Silver	Ag	107.9
Sodium	Na	23.0
Sulphur	S	32.1
Tin	Sn	118.7
Zinc	Zn	65.4

Concept of Average Atomic Mass

The word average has been used in the above definition and is very significant. It has been found that the majority of the elements occur in nature as mixtures of several isotopes. **Isotopes** *are the different atoms of the same element possessing different atomic masses but same atomic number.* The atomic mass of such an element is the average of the atomic masses of the naturally occurring isotopes of the element taking into account their relative abundance. This is called **average atomic mass.**

For example, carbon occurs as three isotopes with relative abundances and masses as :

Isotope	Relative abundance (%)	Atomic mass (amu)
^{12}C	98.892	12
^{13}C	1.108	13.00335
^{14}C	2×10^{-10}	14.00317

Therefore, average atomic mass of carbon

$$= \frac{98.892 \times 12 + 1.108 \times 13.00335 + 2 \times 10^{-10} \times 14.00317}{100}$$

= **12.001 u**

Similarly, chlorine occurs in nature in the form of two isotopes with atomic mass 35 and 37 in the ratio of 3 : 1 respectively. Therefore,

$$\text{Average atomic mass of chlorine} = \frac{35 \times 3 + 37 \times 1}{3 + 1} = 35.5 \text{ u}$$

Thus, we say that on an average, an atom of chlorine is 35.5 times heavier than 1/12th of the mass of a carbon atom (C^{12}).

Similarly, neon occurs as three isotopes and their relative abundance are as follows :

Isotope	Fractional abundance
^{20}Ne	0.9051
^{21}Ne	0.0027
^{22}Ne	0.0922

Average atomic mass of neon

= 20 × 0.9051 + 21 × 0.0027 + 22 × 0.0922

= 20.179 u

Since the atomic mass is the ratio of the masses, it has no units. However, we express it as a.m.u., which only signifies that it is taken on atomic mass unit scale in which 1/12th of carbon atom is fixed as 1 u.

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SOLVED EXAMPLES

Example 26.

Calculate the atomic mass of naturally occurring argon from the following data :

Isotope	Isotopic mass (g mol^{-1})	abundance
^{36}Ar	35.96755	0.337%
^{38}Ar	37.96272	0.063%
^{40}Ar	39.9624	99.600%

N.C.E.R.T.

Solution: Average atomic mass of argon

$$= \frac{35.96755 \times 0.337 + 37.96272 \times 0.063 + 39.9624 \times 99.60}{100}$$

$$= \mathbf{39.948 g\ mol^{-1}}$$

Example 27.

Boron occurs in nature in the form of two isotopes having atomic mass 10 and 11. What are the percentage abundances of two isotopes in a sample of boron having averge atomic mass 10.8 ?

Solution: Let the % abundance of ^{10}B isotope = x

Then % abudance of ^{11}B isotope = $100 - x$

The average atomic mass = $\frac{x \times 10 + (100 - x) \times 11}{100}$

But, average atomic mass = 10.8

$$\therefore \quad \frac{x \times 10 + (100 - x) \times 11}{100} = 10.8$$

or $\quad 10x + 1100 - 11x = 10.8 \times 100$

$$-x = -1100 + 1080$$

or $\quad x = 20$

Thus, percentage abundance; ^{10}B = 20, ^{11}B = 80

Gram Atomic Mass or Gram Atom

The atomic mass of an element expressed in grams is called **gram atomic mass.** *This amount of the element* is also called **one gram atom.** For example, the atomic mass of hydrogen is 1.008 a.m.u. and thus, gram atomic mass or a gram atom of hydrogen is 1.008 g.

Similarly, the atomic mass of oxygen = 16 a.m.u.

Therefore, gram atomic mass of oxygen = 16 g

However, the term *gram atom should not be confused with mass of one atom of the element*. For example, the mass of one atom of oxygen is only 2.66×10^{-23} g whereas, the gram atom of it (which is also the atomic mass of oxygen in grams) is 16 g. The mass of one atom of an element is known as **actual mass** of the atom.

Molecular Mass

Like atoms, the actual masses of molecules are also very small and cannot be measured by actual weighing. Like atomic masses, molecular masses are expressed relative to the stable isotope of carbon (^{12}C) having mass number 12. Thus,

Molecular mass of a substance may be defined as

the average relative mass of its molecule as compared to the mass of an atom of carbon (^{12}C) taken as 12.

In other words, molecular mass expresses as to how many times a molecule of the substance is heavier than 1/12th of the mass of an atom of carbon. For example, a molecule of carbon dioxide is 44 atom. Therefore, the molecular mass of carbon dioxide (CO_2) is 44 a.m.u.

Molecular mass from atomic masses. The molecular mass may be calculated as the sum of the atomic masses of all the atoms in a molecule. For example,

Molecular mass of methane (CH_4)

= At. mass of C + 4 × At. mass of H

= 12.001 + 4 × 1.008

= **16.033 u**

For simplicity, we may take rounded values of atomic masses of elements such as C = 12, H = 1, O = 16, ... so on.

Molecular mass of carbon dioxide (CO_2)

= At. mass of C + 2 × At. mass of O

= 12 + 2 × 16 = **44 u.**

Similarly,

Molecular mass of H_2SO_4 = 2 × Atomic mass of H + Atomic mass of S + 4 × Atomic mass of O

= 2 × 1 + 32 + 4 × 16

= **98 u**

Molecular mass of sucrose ($C_{12}H_{22}O_{11}$)

= 12 × Atomic mass of C + 22 × Atomic mass of H + 11 × Atomic mass of O

= 12 × 12 + 22 × 1 + 11 × 16

= **342 u**

Like atomic mass, molecular mass is expressed as a.m.u. which only signifies that it is taken on atomic mass unit scale.

Gram Molecular Mass or Gram Molecule

The molecular mass of a substance expressed in grams is called **gram molecular mass.** This amount of a substance is also known as **one gram molecule.** For example, the molecular mass of oxygen is 32 and, therefore, its gram molecular mass or gram molecule is 32 g.

It may be noted that the gram molecular mass may simply be taken as the *molecular mass expressed in grams*. However, this should not be confused with the mass of one molecule of the substance in grams. For example, the mass of one molecule of oxygen is only 5.32×10^{-23} g, whereas the gram molecular mass, which is the mass in grams equal to molecular mass, is 32 g. *The mass of one molecule of a substance, is known as its* **actual mass** of the molecule.

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LEARNING PLUS

Formula mass

Some substances such as sodium chloride, potassium chloride (ionic compounds) do not have discrete molecules as their constituent units. In such compounds, positive (sodium) and negative (chloride) ions are arranged in a three dimensional structure. In this structure, it has been observed that each Na^+ ion is octahedrally surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions. The structure of NaCl is shown below in Fig. 11.

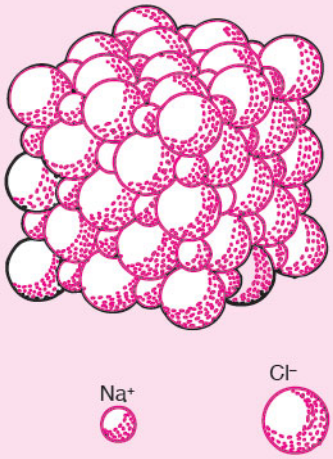

Fig. 11. Structure of NaCl.

In these compounds, we call formula unit (rather than molecular formula) which gives the simple ratio between various ions present. So, for these compounds we use **formula mass** instead of molecular mass. Formula mass is the sum of atomic masses of all atoms in a formula unit of the compound. For example,

Formula mass of sodium chloride
= At. mass of Na + At. mass of Cl
= 23.0 + 35.5
= 58.5 u.

It may be **remembered** that

Gram atomic mass
= Atomic mass expressed in grams
= gram atom

Gram molecular mass
= Molecular mass expressed in grams
= gram molecule

e.g., Gram atomic mass of oxygen or gram atom of oxygen = 16 g

Gram molecular mass of oxygen (O_2) or gram molecule = 32 g

SOLVED EXAMPLES

Example 28.

Calculate
(a) mass of 1.5 gram atoms of calcium (at. mass = 40)
(b) gram atoms in 12.8 g of oxygen (at. mass = 16).

Solution:
(a) 1 gram atom of calcium = 40 g
1.5 gram atoms of calcium = 40 × 1.5 = **60 g**
(b) 1 gram atom of oxygen = 16 g
16 g of oxygen = 1 gram atom

$$12.8 \text{ g of oxygen} = \frac{1}{16} \times 12.8$$

= 0.8 gram atom

Example 29.

(a) Calculate the gram molecular mass of sugar having molecular formula $C_{12}H_{22}O_{11}$
(b) Calculate
(i) the mass of 0.5 gram molecule of sugar and
(ii) Gram molecule of sugar in 547.2 gram.

Solution: (a) Molecular mass of sugar ($C_{12}H_{22}O_{11}$)
= 12 × at. mass of C + 22 × at. mass of H + 11 × at. mass of O
= 12 × 12 + 22 × 1 + 11 × 16 = 342
∴ Gram molecular mass of sugar = 324 g
(b) (i) 1 gram molecule of sugar = 342 g
∴ 0.5 gram molecule of sugar = 342 × 0.5
= 171 g
(ii) 342 g of sugar = 1 gram molecule

$$547.2 \text{ g of sugar} = \frac{1}{342} \times 547.2$$

= 1.6 gram molecule

Example 30.

Calculate the molecular mass of glucose ($C_6H_{12}O_6$) molecule. Given at. masses :
H = 1.008 amu, C = 12.011 amu, O = 16.0 amu.

N.C.E.R.T.

Solution: Molecular mass of glucose ($C_6H_{12}O_6$)
= 6 × At. mass of C + 12 × At. mass of H + 6 × At. mass O
= 6 × (12.011) + 12 × (1.008) + 6 × (16.00)
= 180.162 amu

Example 31.

Calculate
(a) mass of 2.6 gram molecule of SO_2.
(b) number of gram molecules of water in a beaker containing 576 g of water.

Solution: (i) Molecular mass of SO_2 = Atomic mass of S + 2 × Atomic mass of O
= 32 + 2 × 16 = 64
1 gram molecule of SO_2 = 64 g

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2.6 gram molecules of SO_2 = 64 × 2.6 = 166.4 g

(*ii*) Molecular mass of H_2O = 2 × 1 + 16 = 18

∴ 18 g of water = 1 gram molecule

No. of gram molecules in 576 g = $\frac{1}{18} \times 576 = \mathbf{32}$

Practice Problems

30. The relative abundance of various isotopes of silicon is as Si (28) = 92.25%, Si (29) = 4.65% and Si (30) = 3.10%. Calculate the average atomic mass of silicon.

31. Calculate the mass of (*a*) 1.6 gram atoms of oxygen (*b*) 5.6 gram atoms of sulphur (*c*) 2.4 gram atoms of iodine.

(Atomic masses : O = 16, S = 32, I = 127)

32. Calculate the mass of

(*i*)2.5 gram molecules of H_2S, (*ii*) 3.6 gram molecules of glucose ($C_6H_{12}O_6$)

33. Calculate the number of

(*i*) gram atoms in 669.6 g of iron (at. mass = 55.8)

(*ii*) gram molecules in 73.6 g of C_2H_5OH.

34. Which of the following has maximum mass

(*a*) 2.6 gram atoms of sulphur (*b*) 2.6 gram molecules of sucrose ($C_{12}H_{22}O_{11}$) (*c*) 2.6 g of iodine

Answers to Practice Problems

30. 28.11 u.

31. (*a*) 25.6 g (*b*) 179.2 g (*c*) 304.8 g

32. (*i*) 85 g (*ii*) 648 g

33. (*i*) 12 (*ii*) 1.6

34. (*b*)

Hints & Solutions on page 79

MOLE CONCEPT

Quite commonly, we use different units for counting such as dozen for 12 articles, score for 20 articles and gross for 144 articles, irrespective of their nature. For example, one dozen books means 12 books whereas, one dozen apples means 12 apples. In a similar way, chemists use the unit mole for counting atoms, molecules, ions, etc. A mole is a collection of 6.022×10^{23} particles. Thus,

a mole represents 6.022×10^{23} particles

The number 6.022×10^{23} is called **Avogadro number or Avogadro constant**. It is denoted by N_A in honour of nineteenth century Italian scientist, Amedeo Avogadro. In other words, *a mole is an Avogadro number of particles.* For example,

1 mole of hydrogen atoms = 6.022×10^{23} hydrogen atoms.

1 mole of hydrogen molecules = 6.022×10^{23} hydrogen molecules.

1 mole of sodium ions = 6.022×10^{23} sodium ions.

1 mole of electrons = 6.022×10^{23} electrons.

It may be noted that the exact value of Avogadro number, N_A is 6.022137×10^{23}. However, in most of the calculations the value 6.022×10^{23} entities/mol for N_A is generally used.

A curious question comes to our mind. Why did chemists choose the number 6.022×10^{23} for a mole ? This seems to be very odd choice ? They would have selected simple number such as 10^3 (one thousand), 10^6 (one million), 10^{10}, 10^{20} or 10^{50}. However, this choice is based on the fact that chemists preferred the definition in *terms of a quantity that can be measured easily.* We have learnt that atoms and molecules are so small that we cannot see them even with a powerful microscope. Therefore, it is very difficult to count the actual number of atoms or molecules in a given sample of substance. Thus, weighing is easier than direct counting when the number of particles to be counted is very large. A mole was, therefore, originally defined in terms of mass. On this basis, chemists selected a standard number, which is equal to the number of atoms present in exactly 12.0 g of carbon (^{12}C).

Thus, a **mole** is defined as

the amount of substance that contains as many particles or entities (atoms, molecules or ions), as there are atoms in exactly 12 g (or 0.012 kg) of carbon-12 isotope.

In order to determine the number of atoms in 12 g of C-12, the mass of a carbon-12 was determined by a mass spectrometer. It was found to be equal to 1.992648×10^{-23} g. Knowing that 1 mol of carbon weights 12 g, the number of atoms in 1 mol of C-12 is

$$= \frac{12 \text{ g/mol of C} - 12}{1.992648 \times 10^{-23} \text{ g/atom of C}}$$

$$= 6.022137 \times 10^{23} \text{ atoms/mol}$$

Thus, we can say that a mole has 6.022137×10^{23} entities (atoms, molecules or ions, etc.). For simplicity, its value may be given equal to 6.022×10^{23} or Avogadro constant.

WATCH OUT !

It may be noted that while using the term mole, it is essential to specify the kind of particles involved. In case of certain substances, it is not clear whether we are talking of 1 mol atom or 1 mol molecule. If we simply say 1 mol of hydrogen, it means we are talking of naturally occurring form of hydrogen *i.e.*, H_2. So, 1 mol of hydrogen means 1 mole of hydrogen

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molecules. Consequently, to avoid confusion, we must be careful to specify the kind of particles when the term mole is used. For example, one mole of oxygen atoms contains 6.022×10^{23} atoms but one mole of oxygen molecules (O_2) contains 6.022×10^{23} molecules. Therefore, a mole of oxygen molecules is equal to two moles of oxygen atoms. However, if it is not mentioned, then we should consider that it is the natural form of that substance. These days, the molecular forms of hydrogen, nitrogen and oxygen are called dinitrogen (N_2), dihydrogen (H_2) and dioxygen (O_2) respectively to avoid confusion.

SOLVED EXAMPLES

❑ Example 32.

How many molecules and atoms of sulphur are present in 0.1 mole of S_8 molecules ?

Solution:

1 mol of S_8 molecule $= 6.022 \times 10^{23}$ molecules

$\therefore$ 0.1 mol of S_8 molecules $= 6.022 \times 10^{23} \times 0.1$

$= \mathbf{6.022 \times 10^{22}}$ **molecules**

One molecule of S_8 contains 8 atoms of sulphur

$\therefore$ 6.022×10^{22} molecules of S_8 contain $= 6.022 \times 10^{22} \times 8$

$= \mathbf{4.816 \times 10^{23}}$ **atoms**

❑ Example 33.

Calculate the number of moles of iodine in a sample containing 1.0×10^{22} molecules.

Solution: 6.022×10^{23} molecules of iodine = 1 mol

1.0×10^{22} molecules of iodine

$$= \frac{1}{6.022 \times 10^{23}} \times 1 \times 10^{22}$$

$= \mathbf{0.0166\ mol}$

MASS-MOLE CONVERSIONS

Mole and Gram Atomic Mass

We have learnt that a mole represents amount of substance that contains same number of particles as the number of atoms in 12 g of carbon. But 12 g of carbon also correspond to 1 g atom of carbon (as discussed earlier). Similarly, it has been found that the mass of one mole atoms (6.022×10^{23} atoms) of hydrogen is equal to 1 g (or 1 gram atom of hydrogen). This can also be easily understood as given below.

We know that an atom of carbon is twelve times heavier than an atom of hydrogen. This means that the mass of an atom of hydrogen is 1/12th the mass of a carbon atom. Thus, if 6.022×10^{23} atoms of carbon weigh 12 g, the same number of hydrogen atoms will weigh $12 \times 1/12 = 1$g.

Similarly, the mass of 6.022×10^{23} atoms of oxygen, sodium and argon are 16 g (1 gram atom of oxygen), 23 g (1 gram atom of sodium) and 40 g (1 gram atom of argon) respectively. Thus, it may be concluded that

mass of 6.022×10^{23} atoms (or one mole atoms) of any element in grams is equal to its gram atomic mass or one gram atom.

In other words,

One mole of atoms ≡ 6.022×10^{23} atoms
≡ Gram atomic mass of the element

Mole and Gram Molecular Mass

The mass of 6.022×10^{23} molecules of a substance is equal to its gram molecular mass or gram molecule. For example, the mass of 1 mole molecules (6.022×10^{23} molecules) of water is equal to 18 g (1 gram mole molecules of oxygen is 32 g (1 gram mole of O_2) and that of 6.022×10^{23} molecules of carbon dioxide is 44 g (1 gram mole of CO_2). Thus,

mass of 6.022×10^{23} molecules (or 1 mole molecules) of any substance in grams is equal to its gram molecular mass or one gram molecule.

In other words,

One mole of molecules ≡ 6.022×10^{23} molecules
≡ Gram molecular mass

Mole Concept as applied to Ionic Compounds

It may be noted that the mole concept is also applicable to ionic compounds which do not contain molecules. These are made up of positively and negatively charged ions. In such cases, the formula of an ionic compound does not represent one molecule, but it gives the ratio between the constituent ions. The term mole is also applied for ionic compounds and one mole of formula units means 6.022×10^{23} formula units. The mass of one mole formula units in grams is equal to formula mass expressed in grams or gram formula mass of the compound. Thus,

mass of 6.022×10^{23} formula units (or one mole formula units) of any ionic substance in grams is equal to its gram formula mass.

For example, a mole of NaCl weighs equal to 58.5 g (one gram formula mass) and contains 6.022×10^{23} formula units of NaCl or 6.022×10^{23} Na^+ ions and 6.022×10^{23} Cl^- ions. Similarly, 1 mole of calcium chloride ($CaCl_2$) has mass equal to its gram formula mass *i.e.,* 111 g and contains 6.022×10^{23} Ca^{2+} ions and $2 \times 6.022 \times 10^{23}$ Cl^- ions.

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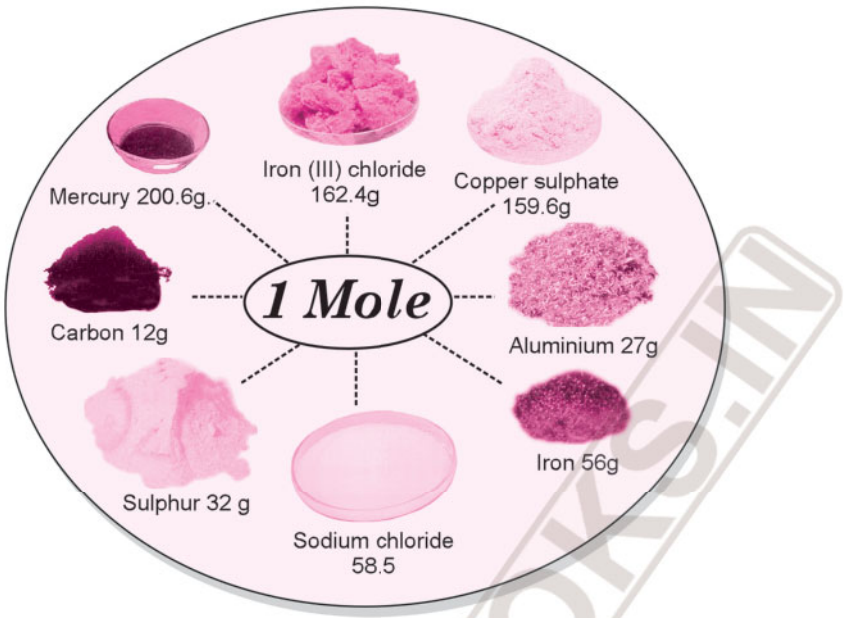
1 mole of some substances (elements and compounds) are shown below :



The mass of 1 mol of a substance is called its **molar mass (M).** The units of molar mass are g mol^{-1} or kg mol^{-1}. Therefore, the molar mass is equal to atomic mass or molecular mass expressed in grams depending upon whether the substance contains atoms or molecules. We have also learnt that 1 mol of a substance contains 6.022×10^{23} entities or particles. Thus, mass of 1 mol of any substance will be its molar mass and it contains 6.022×10^{23} particles of that substance. For example, the molar mass of sodium *atoms* is the mass of 1 mol of sodium atoms, which is 23 g mol^{-1} and it contains 6.022×10^{23} sodium atoms. Similarly, the molar mass of water *molecules* is the mass of 1 mol of water molecules *i.e.,* 18 g mol^{-1} and it contains 6.022×10^{23} water molecules. The molar mass of NaCl is the mass of 1 mol of NaCl formula units *i.e.,* 58.5 g mol^{-1} and it contains 6.022×10^{23} formula units of NaCl.

Mole in Terms of Volume

Mole is also related to the volume of the gaseous substance. Volume of one mole of any substance is called its **molar volume.** The molar volume of solids and liquids can be easily calculated if we know the molar mass and density at any given temperature and pressure because these do not change much with temperature and pressure. However, the molar volumes of gases change considerably with temperature and pressure. It has been observed that one mole of an ideal gas (*i.e.,* 6.022×10^{23} molecules) occupies 22.4 litres at N.T.P. (0°C and 1 atm pressure). For example,

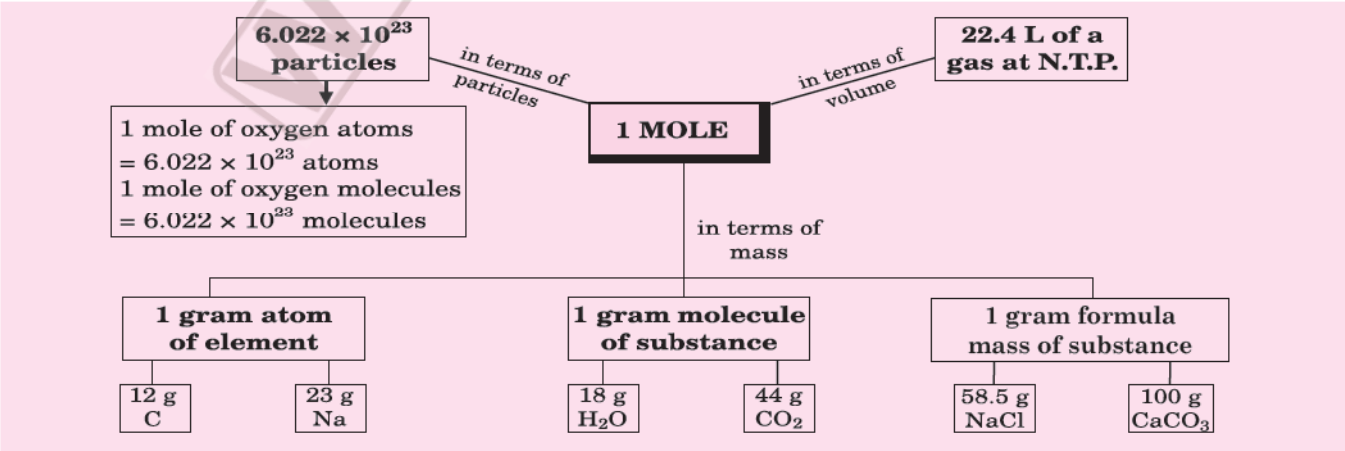
1 mole of hydrogen gas at N.T.P. = 22.4 litres

1 mole of CO_2 gas at N.T.P. = 22.4 litres

This provides us with a method to determine molecular masses (weights) of gases from experimentally determined density as

Molecular mass = Molar volume × Density

The summary of various relationships of mole may be illustrated as shown below :



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These relations may also be **summarised** below :

One mole of atoms = 6.022×10^{23} atoms = Gram atomic mass of the element

Moles of an element = $\frac{\text{Mass of element}}{\text{Atomic mass}}$

Mass of one atom = $\frac{\text{Atomic mass}}{6.022 \times 10^{23}}$

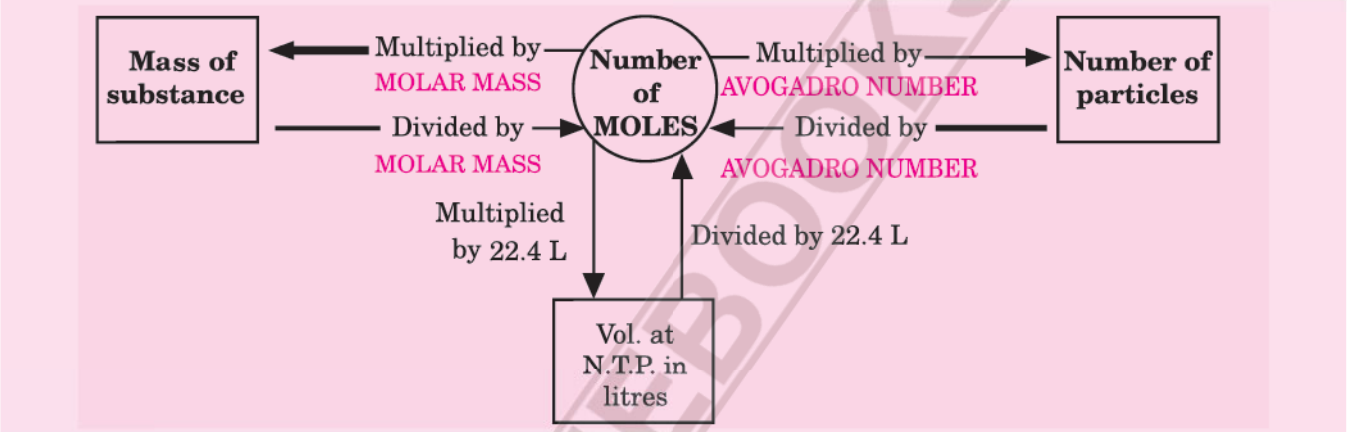
One mole of molecules = 6.022×10^{23} molecules = Gram molecular mass of the substance

Moles of a compound = $\frac{\text{Mass of compound}}{\text{Molecular mass}}$

Mass of one molecule = $\frac{\text{Molecular mass}}{6.022 \times 10^{23}}$

Volume occupied by 1 mole of a gas at N.T.P. = 22.4 L

The scheme for calculation of mole, mass and number of particles can be summarised below :



SOLVED EXAMPLES

Type I. Calculation of mass of atom(s) or molecule(s)

Example 34.

(i) Calculate the mass of an atom of silver (atomic mass = 108).

(ii) 1 molecule of naphthalene ($C_{10}H_8$)

Solution:

(i) Mass of 6.022×10^{23} atoms of silver = 108 g

Mass of 1 atom of silver = $\frac{108}{6.022 \times 10^{23}}$ = **1.793×10^{-22} g**

(ii) Molecular mass of naphthalene ($C_{10}H_8$)
$= 10 \times 12 + 8 \times 1 = 128$

Mass of 6.022×10^{23} molecules of napthalene = 128 g

Mass of 1 molecule of naphthalene = $\frac{128}{6.022 \times 10^{23}}$
= **2.12×10^{-22} g**

Example 35.

Calculate the mass of

(i) 1 atom of ^{14}C

(ii) 1 molecule of N_2

(iii) 1 molecule of water

(iv) 100 molecules of sucrose ($C_{12}H_{22}O_{11}$).

Solution:

(i) 6.022×10^{23} atoms of carbon ≡ Gram atomic mass of carbon (^{14}C) = 14 g

$\therefore$ Mass of 1 atom of ^{14}C = $\frac{14}{6.022 \times 10^{23}}$ = **2.32×10^{-23} g**

(ii) 6.022×10^{23} molecules of N_2 = Gram molecular mass = 28 g

Mass of 1 molecule of N_2 = $\frac{28}{6.022 \times 10^{23}}$ = **4.65×10^{-23} g**

(iii) 6.022×10^{23} molecules of H_2O = Gram molecular mass = 18 g

Mass of 1 molecule of H_2O = $\frac{18}{6.022 \times 10^{23}}$ = **2.99×10^{-23} g**

(iv) 6.022×10^{23} molecules of sucrose = Gram molecular mass = 342 g

Mass of 100 molecules of sucrose = $\frac{342}{6.022 \times 10^{23}} \times 100$
= **5.68×10^{-20} g**

Example 36.

Calculate the mass of 1 u (atomic mass unit) in grams.

Solution: 1 u = $\frac{1}{12}$ th of the mass of carbon atom

Let us calculate the mass of a carbon atom.

6.022×10^{23} atoms of carbon = 12 g

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$$\text{Mass of one carbon atom} = \frac{12}{6.022 \times 10^{23}} = 1.99 \times 10^{-23}\ \text{g}$$

$$\therefore \quad 1\ \text{u} = \frac{1}{12} \times 1.99 \times 10^{-23}\ \text{g} = \mathbf{1.66 \times 10^{-24}\ g}$$

Type II. Calculation of number of molecules present in a given volume of a gas

Example 37.

Calculate the number of molecules and number of atoms present in 11.2 litres of oxygen (O_2) at N.T.P.

Solution: We know that one mole of O_2 at N.T.P. occupies 22.4 litres.

$$11.2 \text{ litres of } O_2 \text{ at N.T.P.} = \frac{1}{22.4} \times 11.2 = 0.5 \text{ mole}$$

Now, 1 mole of O_2 contains $= 6.022 \times 10^{23}$ molecules

0.5 mole of O_2 contains $= 6.022 \times 10^{23} \times 0.5$

$= \mathbf{3.01 \times 10^{23}\ molecules}$

1 molecule of oxygen $= 2 \times 3.01 \times 10^{23}$

$= \mathbf{6.02 \times 10^{23}\ atoms.}$

Example 38.

The mass of 94.5 mL of a gas at S.T.P. is found to be 0.2231 g. Calculate its molecular mass.

Solution:

$$\text{Density of gas} = \frac{\text{Mass}}{\text{Volume}} = \frac{0.2231\ \text{g}}{94.5\ \text{mL}}$$

Molecular mass = Molar volume × Density

Molar volume = 22.4 L = 22.4 × 1000 mL

$$\therefore \text{ Molecular mass} = \frac{22.4 \times 1000 \times 0.2231}{94.5} = \mathbf{52.9}$$

Type III. Converting mass to moles or to atoms/molecules

Example 39.

Calculate the number of moles in the following :

(a) 7.85 g of iron (b) 4.68 mg of silicon (c) 65.6 μg of carbon

N.C.E.R.T.

Solution: (a) 7.85 g of iron

Atomic mass of Fe = 55.8 u

$$\text{Mole of iron} = \frac{\text{Mass of iron}}{\text{Atomic mass}} = \frac{7.85}{55.8} = \mathbf{0.141}\ \text{mol}$$

(b) 4.68 mg of silicon $= 4.68 \times 10^{-3}$ g of silicon

Atomic mass of silicon = 28.1

$$\text{Moles of silicon} = \frac{\text{Mass of silicon}}{\text{Atomic mass}} = \frac{4.68 \times 10^{-3}}{28.1} = \mathbf{1.66 \times 10^{-4}\ mol}$$

(c) 65.6 μg of carbon $= 65.6 \times 10^{-6}$ g of carbon

Atomic mass of carbon = 12

$$\text{Molecules of carbon} = \frac{\text{Mass of carbon}}{\text{Atomic mass}} = \frac{65.6 \times 10^{-6}}{12} = \mathbf{5.47 \times 10^{-6}\ mol}$$

Example 40.

Calculate the number of molecules in a drop of water weighing 0.05 g (H = 1, O = 16).

Solution: Gram molecular mass of H_2O = 18.0 g

18.0 g of H_2O contain $= 6.022 \times 10^{23}$ molecules

$$\therefore \quad 0.05\ \text{g of } H_2O \text{ contain} = \frac{6.022 \times 10^{23} \times 0.05}{18.0} = \mathbf{1.672 \times 10^{21}\ molecules}$$

Example 41.

Calculate the number of atoms in each of the following :

(i) 52 mol of Ar (ii) 52 u of He (iii) 52 g of He.

N.C.E.R.T.

Solution:

(i) 1 mol of Ar contains $= 6.022 \times 10^{23}$ atoms

52 mol of Ar will contain $= 6.022 \times 10^{23} \times 52 = \mathbf{3.13 \times 10^{25}\ atoms}$

(ii) 4 u of He = 1 atom

52 u of He $= \frac{1}{4} \times 52 = \mathbf{13\ atoms}$

(iii) 4 g of He contain $= 6.022 \times 10^{23}$ atoms

52 g of He will contain $= \frac{6.022 \times 10^{23} \times 52}{4} = \mathbf{7.83 \times 10^{24}\ atoms}$

Example 42.

Calculate the number of moles in the following masses :

(i) 1.46 metric tones of Al (1 metric ton = 10^3 kg)

(ii) 7.9 mg of Ca

N.C.E.R.T.

Solution:

(i) 1.6 metric tons of Al $= 1.46 \times 10^3 \times 10^3$ g of Al $= 1.46 \times 10^6$ g

Atomic mass of Al = 27

$$\text{Moles of Al} = \frac{\text{Mass of Al}}{\text{Atomic mass}} = \frac{1.46 \times 10^6}{27} = 5.41 \times 10^4\ \text{mol}$$

(ii) 7.9 mg of Ca $= 7.9 \times 10^{-3}$ g of Ca

Atomic mass of Ca = 40.1

$$\text{Moles of Ca} = \frac{\text{Mass of Ca}}{\text{Atomic mass}} = \frac{7.9 \times 10^{-3}}{40.1} = \mathbf{1.97 \times 10^{-4}\ mol}$$

Example 43.

Suppose the chemists had chosen 10^{20} as the number of particles in a mole. What would be the molecular mass of oxygen gas ?

Solution: According to present concept of mole,

6.022×10^{23} molecules of oxygen weigh = 32 g

$$\therefore \quad \text{Mass of 1 molecule of oxygen} = \frac{32}{6.022 \times 10^{23}} = 5.32 \times 10^{-23}\ \text{g}$$

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If the mole contained 10^{20} particles

The mass of one mole *i.e.*, 10^{20} particles

$= 5.32 \times 10^{-23} \times 10^{20} = 5.32 \times 10^{-3}$ g

$\therefore$ Molecular mass of oxygen = **5.32×10^{-3} g**

❑ Example 44.

Calculate the number of atoms of each type in 5.3 g of Na_2CO_3

Solution:

Gram molecular mass of Na_2CO_3 = $2 \times 32 + 12 + 3 \times 16$ = 106.0 g

106.0 g of Na_2CO_3 = 1 mol

5.3 g of Na_2CO_3 = $\frac{1 \times 5.3}{106.0} = 0.05$ mol

Now, 1 mol of Na_2CO_3 contains = $2 \times 6.022 \times 10^{23}$ sodium atoms

$\therefore$ 0.05 mol of Na_2CO_3 contains = $0.05 \times 2 \times 6.022 \times 10^{23}$ sodium atoms = **6.022×10^{22} Na atoms**

1 mol of Na_2CO_3 contains = 6.022×10^{23} carbon atoms

0.05 mol of Na_2CO_3 contains = $0.05 \times 6.022 \times 10^{23}$ carbon atom = **3.01×10^{22} carbon atoms**

1 mol of Na_2CO_3 contains = 6.022×10^{23} oxygen atoms

$\therefore$ 0.05 mol of Na_2CO_3 contains = $0.05 \times 6.022 \times 10^{23}$ oxygen atoms

$\therefore$ 0.05 mol of Na_2CO_3 contains = $0.05 \times 3 \times 6.022 \times 10^{23}$ oxygen atoms = **9.03×10^{22} oxygen atoms**

❑ Example 45.

Calculate the number of molecules present in
(a)1 kg oxygen,
(b)1 dm^3 of hydrogen at S.T.P.

Solution: (*a*) 1 mole of oxygen or 32 g oxygen contains 6.022×10^{23} molecules of oxygen. Thus,

32 g of oxygen contain molecules = 6.022×10^{23}

1000 g of oxygen contain molecules = $\frac{6.022 \times 10^{23}}{32} \times 1000$

= **1.88×10^{25}**

(*b*) We know that 1 mole of H_2 at S.T.P. occupies 22.4 dm^3 and contains 6.022×10^{23} molecules.

22.4 dm^3 of hydrogen contain molecules = 6.022×10^{23}

1 dm^3 of hydrogen contains molecules = $\frac{6.022 \times 10^{23}}{22.4}$

= **2.69×10^{22}**

❑ Example 46.

Chlorophyll, the green colouring matter of plants contains 2.68% of magnesium by weight. Calculate the number of magnesium atoms in 2.00 g of chlorophyll (at. mass of Mg = 24).

N.C.E.R.T.

Solution: Mass of chlorophyll = 2.0 g

Percentage of Mg = 2.68 g

Mass of Mg in 2.0 g of chlorophyll = $\frac{2.68 \times 2.0}{100}$

= 0.054 g

6.022×10^{23} atoms of magnesium = 24 g

24 g of Mg contains = 6.022×10^{23} atoms

0.054 g of Mg contains = $\frac{6.022 \times 10^{23}}{24} \times 0.054$

= **1.3×10^{21} atoms**

Type IV. Calculation of sizes of individual atoms/ molecules.

❑ Example 47.

Calculate
(a) the actual volume of one molecule of water.
(b) the radius of a water molecule assuming to be spherical (density of water = 1 g ml^{-1}).

Solution:

(*a*) Density of water = 1 g ml^{-1}

$\therefore$ 1 g of H_2O = 1 ml

1 mole of water = 18 g of H_2O = 18 ml of water

$\therefore$ 6.022×10^{23} molecules of water occupy volume = 18ml

1 molecule of water occupy volume = $\frac{18}{6.022 \times 10^{23}}$

= **2.99×10^{-23} mol**

(*b*) Since water molecule is assumed to be spherical, its volume is equal to $\frac{4}{3}\pi r^3$, where r is the radius of water molecule.

$\therefore$ $\frac{4}{3}\pi r^3 = 2.99 \times 10^{-23}$

or $r^3 = \frac{2.99 \times 10^{-23} \times 3}{4 \times 3.143}$ ($\pi = 3.143$)

or $r = \left(\frac{2.99 \times 10^{-23} \times 3}{4 \times 3.143}\right)^{1/3}$

$= (7.13 \times 10^{-24})^{1/3} = 1.925 \times 10^{-8}$ cm

= **1.925 Å**

Type V. Miscellaneous calculations on mole concept

❑ Example 48.

KBr (potassium bromide) contains 32.9% by weight of potassium. If 6.40 g of bromine reacts with 3.60 g of potassium, calculate the number of moles of potassium which combine with bromine to from KBr.

Solution:

Suppose mass of KBr = 100 g

Mass of potassium = 32.9 g

106.0 g of Na_2CO_3 = 1 mol

Mass of bromine = 67.1 g

67.1 g of bromine combine with potassium = 32.9 g

$\therefore$ 6.4 g of bromine will combine with potassium

= $\frac{32.9}{67.1} \times 6.4 = 3.14$ g

Atomic mass of potassium = 39 u

$\therefore$ Moles of potassium which combine with bromine to from KBr = $\frac{3.14}{39}$ = **0.0805 mol**

❑ Example 49.

The cost of table salt (NaCl) and sugar ($C_{12}H_{22}O_{11}$) are ₹ 12 per kg and ₹ 36 per kg respectively. Calculate their cost per mole.

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Solution: (*a*) *Cost of table salt per mole :*

Molecular mass of table salt (NaCl) = 23 + 35.5 = 58.5

Now, 1000 g of NaCl cost = ₹ 12

$\therefore$ 58.5 g of NaCl will cost = $\frac{12}{1000} \times 58.5$ = ₹ 0.702

= **70 paise (approx.)**

(*b*) *Cost of sugar per mole :*

Molecular mass of sugar ($C_{12}H_{22}O_{11}$) = 12 × 12 + 22 × 1 + 11 × 16 = 342

Now, 1000 g of sugar cost = ₹ 36

$\therefore$ 342 g of sugar will cost = $\frac{36}{1000} \times 342$ = ₹ 12.312

= ₹ **12 (approx)**

❑ Example 50.

Silver is a very precious metal and is used in Jewellery. One million atoms of silver weigh 1.79 × 10^{-16} g. Calculate the atomic mass of silver.

Solution: Atomic mass of an element is the mass of 6.022 × 10^{23} atoms.

Now, 10^6 atoms of silver weigh = 1.79 × 10^{-16} g

6.022 × 10^{23} atoms of silver weigh

$$= \frac{1.79 \times 10^{-16} \times 6.022 \times 10^{23}}{10^6} = 107.8 \text{ g}$$

Atomic mass of silver = **107.8**

❑ Example 51.

Calculate the weight of carbon monoxide having same number of oxygen atoms as are present in 88 g of carbon dioxide.

Solution: Molecular mass of CO_2 = 12 + 2 × 16 = 14

1 mole of CO_2 = 44 g

44 g of CO_2 contain = 6.022 × 10^{23} molecules

88 g of CO_2 contain = $\frac{6.022 \times 10^{23} \times 88}{44}$

= 12.044 × 10^{23}

Each molecule of CO_2 contains 2 oxygen atoms

No. of oxygen atoms in 12.046 × 10^{23} molecules of CO_2

= 2 × 12.046 × 10^{23} = 2.4088 × 10^{24}

Now, we are to calculate the mass of CO containing 2.4092 × 10^{24} atoms of oxygen

Mass of CO containing 6.022 × 10^{23} oxygen atoms = 28 g

Mass of CO containing 2.4088 × 10^{24} oxygen atoms

$$= \frac{28}{6.022 \times 10^{23}} \times 2.4088 \times 10^{24} = \mathbf{112\ g}$$

❑ Example 52.

A certain public water supply contained 0.10 parts per billion of chloroform ($CHCl_3$). How many molecules of $CHCl_3$ would be contained in a 0.05 ml drop of this water ?

Solution: Volume = 0.05 ml

Amount of $CHCl_3$ in the drop = $\frac{0.05 \times 0.1}{10^9} = 5.0 \times 10^{-12}$

Molecular mass of $CHCl_3$ = 12 + 1 + 3 × 35.5 = 119.5

Moles of $CHCl_3$ present = $\frac{5.0 \times 10^{-12}}{119.5}$

Molecules of $CHCl_3$ present in the drop

$$= \frac{5.0 \times 10^{-12}}{119.5} \times 6.022 \times 10^{23} = \mathbf{2.5 \times 10^{10}}.$$

❑ Example 53.

Oxygen and nitrogen are present in a mixture in the ratio of 1 : 4 by weight. Calculate the ratio between their molecules.

Solution: Let wt. of given mixture = Wg

Amount of O_2 in mixture = $\frac{W \times 1}{5} = \frac{W}{5}$ g

Amount of N_2 in mixture = $\frac{W \times 4}{5} = \frac{4W}{5}$ g

Moles of O_2 = $\frac{W}{5 \times 32}$

Molecules of O_2 = $\frac{W}{5 \times 32} \times 6.022 \times 10^{23}$

Moles of N_2 = $\frac{4W}{5 \times 28}$

Molecules of N_2 = $\frac{4W}{5 \times 28} \times 6.022 \times 10^{23}$

Ratio of molecules of O_2 and N_2

$$\frac{W}{5 \times 32} \times 6.022 \times 10^{23} : \frac{4W}{5 \times 28} \times 6.022 \times 10^{23}$$

$$\frac{1}{32} : \frac{1}{7}$$

7 : 32.

Practice Problems

35. Calculate the mass of

(*i*) one atom of calcium

(*ii*) one molecule of sulphur dioxide (SO_2).

36. Calculate the number of atoms in

(*i*) 0.5 mole atoms of carbon (C^{12})

(*ii*) 3.2 g of sulphur

(*iii*) 18.0 g of glucose ($C_6H_{12}O_6$)

(*iv*) 0.20 mole molecules of oxygen.

37. Calculate the mass of sodium which contains same number of atoms as are present in 15 g of calcium (at. mass of Ca = 40, Na = 23).

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38. What volume is occupied at N.T.P. by
(*i*) 1.4 g of nitrogen
(*ii*) 6.023×10^{21} molecules of oxygen
(*iii*) 0.2 mole of ammonia ?

39. How many years it would take to spend Avogadro number of rupees at the rate of 10 lakh rupees per second ?

40. One atom of an element 'X' weighs 6.644×10^{-23} g. Calculate the number of gram atoms in 80 kg of it.

41. Calculate the number of molecules and number of atoms present in 5.60 L of ozone (O_3) at N.T.P.

42. Calculate the number of gold atoms in 300 mg of a gold ring of 20 carat gold (atomic mass of gold = 197, pure gold is 24 carat).

43. What mass in kilogram of K_2O contains the same number of moles of K atoms as are present in 1.0 kg of KCl ?

44. How many molecules of water of hydration are present in 630 mg of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) ?

45. How many molecules of CO_2 are present in one litre of air containing 0.03% by volume of CO_2 at STP ?

46. A dot '.' containing carbon has 1 microgram weight. Calculate number of carbon atoms used to make the dot.

47. How many litres of liquid CCl_4 (d = 1.5 g/cc) must be measured out to contain 1×10^{25} Cl atoms ?

48. Calculate the difference in the number of carbon atoms in 1.0 g of C-14 isotope and 1.0 g of C-12 isotope.

49. Calculate the mass of oxygen in grams present in 0.1 mole of $Na_2CO_3.10H_2O$.

Answers to Practice Problems

35. (*i*) 6.64×10^{-23} g (*ii*) 1.06×10^{-22} g
36. (*i*) 3.011×10^{23} atoms (*ii*) 6.022×10^{22} atoms
(*iii*) 1.445×10^{24} atoms (*iv*) 2.409×10^{23} atoms
37. 8.624 g
38. (*i*) 1.12 L (*ii*) 0.224 L (*iii*) 4.48 L
39. 1.91×10^{10} years **40.** 1999.5 gram atoms
41. 1.506×10^{23} molecules, 4.518×10^{23} atoms.
42. 7.64×10^{20} **43.** 0.631 kg
44. 6.022×10^{21} molecules **45.** 8.07×10^{18} molecules
46. 5.019×10^{16} atoms **47.** 0.426 litres
48. 7.2×10^{21} **49.** 20.8 g.

Hints & Solutions on page 79

add on

Conceptual Questions 2

CONCEPTUAL QA

Q. 1. Calculate the total number of electrons present in 1.6 g of methane.

Ans. 16 g of methane contains = 6.022×10^{23} molecules

$$1.6 \text{ g of methane contains} = \frac{6.022 \times 10^{23} \times 1.6}{16}$$
$$= 6.022 \times 10^{22} \text{ molecules}$$
$$\text{One molecule of } CH_4 \text{ contains} = 6 + 4 = 10 \text{ electrons}$$
$$\text{No. of electrons in 1.6 g of methane} = 6.022 \times 10^{22} \times 10$$
$$= 6.022 \times 10^{23}.$$

Q.2. How many molecules of aspirin (molar mass = 180 amu) are present in 50 mg tablet ?

Ans. Molecules of aspirin = $\frac{50 \times 10^{-3}}{180} \times 6.022 \times 10^{23} = 1.673 \times 10^{20}$.

Q.3. Lithium exists in nature in the form of two isotopes, Li-6 and Li-7 with atomic masses 6.015 μ and 7.016 μ and the percentages 8.24 and 91.76 respectively. Calculate the average atomic mass of Li.

Ans. Average atomic mass of Li = $\frac{6.015 \times 8.24 + 7.016 \times 91.76}{100} = 6.934\,\mu$

Q. 4. What is the ratio of molecules between 1 mole of H_2O and 1 mole of sucrose ($C_{12}H_{22}O_{11}$) ?

Ans. 1 : 1

Q. 5. If atomic weight of C and S are 12 and 32 respectively, then an atom of S is ..... time heavier than an atom of C.

Ans. 8/3.

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Q. 6. What is the mass of a mole of water containing 50% of heavy water (D_2O) ?

Ans. 19 g

Q. 7. What is the mass of a molecule of carbon-14 dioxide ($^{14}CO_2$) ?

Ans. $= 7.64 \times 10^{-23}$ g.

Q. 8. Why do atomic masses of most of the elements in atomic mass units involve fraction ?

Ans. This is because atomic mass of an element is the average relative mass of its various isotopes. While taking average, the result comes out to be fraction.

Q.9. What is the approximate molecular mass of dry air containing 78% N_2 and 22% O_2 ?

Ans. Molecular mass = $28 \times 0.78 + 32 \times 0.22 = 28.88$.

Q.10. ^{35}Cl and ^{37}Cl are the naturally occurring isotopes of chlorine. What percentage distribution accounts for the atomic mass 35.45 ?

Ans. Let fraction of $^{35}C = x$, $\therefore$ Fraction of $^{37}C = 1 - x$

$\therefore$ Atomic mass $= x\,(35) + (1.0 - x)\,37 = 35.45$

$\therefore$ $x = 0.775$

$\therefore$ $^{35}Cl = 77.5\%$ and $^{37}Cl = 22.5\%$

Q. 11. Two bulbs A and B of equal capacity contain 10g of oxygen (O_2) and ozone (O_3) respectively. Which bulb will have

(*i*) larger number of molecules?

(*ii*) larger number of oxygen atoms?

Ans. 10g of $O_2 = \frac{10}{32}$ mol $= \frac{10}{32} \times 6.022 \times 10^{23}$ molecules $= 1.88 \times 10^{23}$ molecules

or $= 2 \times 1.88 \times 10^{23}$ O-atoms $= 3.76 \times 10^{23}$ O-atoms

10g of $O_3 = \frac{10}{48}$ mol $= \frac{10}{48} \times 6.022 \times 10^{23}$ molecules $= 1.254 \times 10^{23}$ molecules

or $= 3 \times 1.254 \times 10^{23}$ O-atoms $= 3.76 \times 10^{23}$ O-atoms

(*i*) Bulb A contain larger number of molecules

(*ii*) Both bulbs contain the same number of O-atoms.

Q. 12. In three moles of ethane (C_2H_6) calculate the following :

(*i*) Number of moles of carbon

(*ii*) Number of moles of hydrogen atoms

(*iii*) Number of molecules of ethane

Ans. (*i*) 1 mole of C_2H_6 contains 2 moles of carbon

$\therefore$ Number of moles of carbon in 3 moles of $C_2H_6 = 6$

(*ii*) 1 mole of C_2H_6 contains 6 moles atoms of hydrogen

$\therefore$ Number of moles of hydrogen atoms in 3 mole of $C_2H_6 = 3 \times 6 = 18$

(*iii*) 1 mole of $C_2H_6 = 6.022 \times 10^{23}$ molecules

$\therefore$ Number of molecules in 3 moles of $C_2H_6 = 3 \times 6.022 \times 10^{23}$

$= \mathbf{1.807 \times 10^{24}}$ **molecules**

Q. 13. Which one of the following will have largest number of atoms ?

(*i*) 1 g Au (*s*) (*ii*) 1 g Na (*s*) (*iii*) 1 g Li (*s*) (*iv*) 1 g Cl_2 (*g*)

(at. mass : Au = 197, Na = 23, Li = 7, Cl = 35.5) ***(NCERT)***

Ans. No. of atoms can be calculated as :

(*i*) 1 g Au $= \frac{1}{197} \times 6.022 \times 10^{23} = \frac{6.022}{197} \times 10^{23}$

(*ii*) 1 g Na $= \frac{6.022}{23} \times 10^{23}$

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CONCEPTUAL QA

(*iii*) 1 g Li $= \dfrac{6.022\times10^{23}}{7}$

(*iv*) 1 g Cl_2 $= \dfrac{2\times6.022\times10^{23}}{71} = \dfrac{6.022\times10^{23}}{35.5}$

It is clear that 1 g Li contains largest number of atoms.

Q.14. Calculate the average atomic mass of chlorine using the following data.

	% Natural abundance	Molar mass
^{35}Cl	75.77	34.9689
^{37}Cl	24.23	36.9659

Ans. Average atomic mass $= \dfrac{34.9689\times75.77+36.9659\times24.23}{75.77+24.23}$

$= 26.49 + 8.96$

$= \mathbf{35.45}$

Advanced Level PROBLEMS *Accelerate Your Potential (for JEE Advance)*

Problem 1. An alloy of metals X and Y weighs 12 g and contains atoms X and Y in the ratio of 2 : 5. The percentage by mass of X in the sample is 20. If atomic mass of X is 40, what is the atomic mass of metal Y ?

Solution Mass of metal X in alloy $= \dfrac{12\times20}{100} = 2.40\,g$

Mass of metal Y in alloy $= 12 - 2.4 = 9.6$ g

Number of atoms of X $= \dfrac{6.022\times10^{23}\times2.4}{40}$

$= 3.61\times10^{22}$

Ratio of atoms of X and Y = 2 : 5

No. of atoms of Y $= \dfrac{3.61\times10^{22}\times5}{2}$

$= 9.025\times10^{22}$ atoms

Now, 9.025×10^{22} atoms of Y are present in 9.6 g

6.022×10^{23} atoms of Y are present in

$\dfrac{9.6}{9.025\times10^{22}}\times6.022\times10^{23}$

$= 64.0$ g

$\therefore$ Atomic mass of Y = **64 a.m.u.**

Problem 2. Calculate (*i*) the total number of neutrons and (*ii*) total mass of neutrons in 7 mg of C^{14} (assume mass of neutron = mass of hydrogen atom).

Solution 1 mol of C^{14} = 14 g

or 14 g of C^{14} = 1 mol

7×10^{-3} g of C^{14} $= \dfrac{1}{14}\times7\times10^{-3} = 0.5\times10^{-3}$ mol

Now, 1 mol of C^{14} contains = 6.022×10^{23} atoms

0.5×10^{-3} mol of C^{14} contains

$= 6.022\times10^{23}\times0.5\times10^{-3}$

$= 3.011\times10^{20}$ atoms

No. of electrons in C^{14} = 6

No. of protons in 1 atom of C^{14} = 6

$\therefore$ No. of neutrons in 1 atom of $C^{14} = 14 - 6 = 8$

(*i*) 3.011×10^{20} atoms of C^{14} contain

$= 8\times3.011\times10^{20}$

$= \mathbf{2.409\times10^{21}}$ **neutrons**

(*ii*) Mass of one neutron = Mass of H atom

$= \dfrac{1}{6.022\times10^{23}}$

Mass of 2.409×10^{21} neutrons

$= \dfrac{1}{6.022\times10^{23}}\times2.409\times10^{21}$

$= 4\times10^{-3}$ g = **4 mg.**

Problem 3. Calculate the number of molecules of carbon dioxide present in 300 mL of gas at 273K and 2.5 atm pressure.

Solution First of all, we have to calculate the volume of gas at STP by applying gas equation.

Given conditions	At STP
V_1 = 300 mL	V_2 = ?
T_1 = 273 K	T_2 = 273 K
p_1 = 2.5 atm	p_2 = 1 atm

Applying gas equation, $\dfrac{p_1V_1}{T_1} = \dfrac{p_2V_2}{T_2}$

$\dfrac{2.5\times300}{273} = \dfrac{1\times V_2}{273}$

$\therefore$ $V_2 = 2.5\times300 = 750$ mL

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We know that 1 mol of a gas at STP occupies 22400 mL and contains 6.022×10^{23} molecules

$\therefore$ 750 mL of CO_2 at STP will contain

$$= \frac{6.022 \times 10^{23}}{22400} \times 750$$

$$= \mathbf{2.01 \times 10^{22}\ molecules}$$

Problem 4. If atomic mass of carbon was taken as 100 u, then what would be the value of Avogadro's number?

Solution Avogadro number would be the number of atoms in 100 g of carbon.

12 g of carbon contain 6.022×10^{23} atoms

then 100 g of carbon would contain atoms

$$= \frac{6.022 \times 10^{23} \times 100}{12}$$

$$= \mathbf{5.01 \times 10^{24}\ atoms}$$

Problem 5. A 0.005 cm thick coating of copper is deposited on a plate of 0.5 m^2 total area. Calculate the number of copper atoms deposited on the plate (density of copper = 7.2 g cm^{-3}, atomic mass = 63.5).

Solution Area of plate = 0.5 m^2 = 0.5×10^4 cm^2

Thickness of coating = 0.005 cm

Volume of copper deposited = $0.5 \times 10^4 \times 0.005$

= 25 cm^3

Mass of copper deposited = $25 \times 7.2 = 180$ g

Now, 63.5 g of copper contain atoms = 6.022×10^{23}

180 g of copper contain atoms = $\frac{6.022 \times 10^{23}}{63.5} \times 180$

$$= \mathbf{1.71 \times 10^{24}\ atoms}$$

Problem 6. Calculate the number of molecules present in a spherical drop of water having a radius 1 mm if density of water is 1 g cm^{-3}.

Solution Since water molecule is assumed to be spherical, its volume is equal to $\frac{4}{3}\pi r^3$ where r is the radius of water molecule.

Radius = 1 mm = 0.1 cm

$$\text{Volume} = \frac{4}{3}\pi(0.1)^3$$

$$= \frac{4}{3} \times 3.143 \times 0.001 = 0.00419\ cm^3$$

Mass of drop of water = Volume × Density

= 0.00419 cm^3 × 1 g cm^{-3} = 0.0419 g

Now, 1 mole of water = 18 g of water contain 6.022×10^{23} molecules.

$\therefore$ 0.00419 g of water contain molecules

$$= \frac{6.022 \times 10^{23}}{18} \times 0.00419$$

$$= \mathbf{1.40 \times 10^{20}}$$

Problem 7. 1×10^{21} molecules are removed from 280 mg of carbon monoxide. Calculate the number of moles of carbon monoxide left.

Solution **Step I.** *To calculate the number of moles of carbon monoxide in 280 mg.*

$$\text{No. of moles of CO} = \frac{\text{Wt. of CO in grams}}{\text{Gram molecular mass of CO}}$$

$$= \frac{280}{1000} \times \frac{1}{28} = 0.01 \text{ mol.}$$

Step II. *To calculate the number of moles of carbon monoxide left.*

6.022×10^{23} molecules of CO = 1 mol.

1×10^{21} molecules of CO

$$= \frac{1 \times 10^{21}}{6.022 \times 10^{23}} = 0.0016 \text{ mol.}$$

No. of moles of CO left =

No. of moles of CO taken – No. of moles of CO removed

= 0.01 – 0.0016 = 0.0084

= **8.4×10^{-3} mol.**

PERCENTAGE COMPOSITION AND MOLECULAR FORMULA

To determine the molecular formula of a compound, we begin by measuring the mass or mass percentage of each element present in the compound. The composition is generally expressed as the **mass percentage composition.**

Mass percentage

gives the mass of each element expressed as the percentage of the total mass.

In other words, it gives the number of grams of the element present in 100 g of the compound. It is obtained by dividing the mass of each element in 1 mole of the compound by molar mass of the compound and multiplying by 100. Thus,

Mass percentage of an element

$$= \frac{\text{Mass of that element in 1 mole compound}}{\text{Molar mass of compound}} \times 100$$

For example, let us calculate the mass percentage composition of glucose ($C_6H_{12}O_6$)

The formula of glucose = $C_6H_{12}O_6$

Molar mass of glucose = $6 \times 12 + 12 \times 1 + 6 \times 16 = 180$

The formula of glucose shows that there are 6 C atoms, 12 H atoms and 6 O atoms.

Mass of C = $6 \times 12 = 72$

$$\text{Mass percentage of C} = \frac{72}{180} \times 100 = \mathbf{40.0\%}$$

Mass of H = $12 \times 1 = 12$

$$\text{Mass percenatage of H} = \frac{12}{180} \times 100 = \mathbf{6.67\%}$$

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Mass of O = 6 × 16 = 96

$$\text{Mass percentage of O} = \frac{96}{180} \times 100 = \mathbf{53.33\%}$$

Similarly, mass percentage of ammonia (NH_3) can be calculated as :

Molar mass of NH_3 = 14 + 3 = 17

The formula of NH_3 shows that there are 1 N atom and 3 H atoms

$$\text{Mass percentage of N} = \frac{\text{Mass of N in 1 mol of } NH_3}{\text{Molar mass of } NH_3} \times 100$$

$$= \frac{14}{17} \times 100 = 82.35\%$$

$$\text{Mass percentage of H} = \frac{\text{Mass of H in 1 mol of } NH_3}{\text{Molar mass of } NH_3} \times 100$$

$$= \frac{3}{17} \times 100 = 17.65\%$$

Let us consider one more example of ethanol having the molecular formula C_2H_5OH. Molar mass of ethanol = 2 × 12 + 6 × 1 × 16 = 46 g

Mass of C = 2 × 12 = 24

$$\text{Mass \% of C} = \frac{24}{46} \times 100 = 52.17\%$$

Mass of H = 6 × 1

$$\text{Mass \% of H} = \frac{6}{46} \times 100 = 13.04\%$$

Mass of O atom = 16.0

$$\text{Mass \% of O} = \frac{16}{46} \times 100 = 34.78\%$$

SOLVED EXAMPLES

Example 54.

Calculate the mass percentage composition of copper pyrites ($CuFeS_2$).

Solution: Molar mass of $CuFeS_2$

= 63.5 + 55.8 + 2 × 32 = 183.3

Mass of Cu = 63.5

$$\text{Mass percentage of Cu} = \frac{63.5}{183.3} \times 100 = 34.64\%$$

Mass of iron = 55.8

$$\text{Mass percentage of iron} = \frac{58.5}{183.3} \times 100 = 30.44\%$$

Mass of sulphur = 2 × 32 = 64

$$\text{Mass percentage of sulphur} = \frac{64}{183.3} \times 100$$

$$= \mathbf{34.91\%}$$

Example 55.

Calculate the percentage composition of the following compounds:

(i) Urea $CO(NH_2)_2$

(ii) Copper sulphate $CuSO_4.5H_2O$.

Solution: (*i*) Urea : $CO(NH_2)_2$

Molar mass of urea = 12 + 16 + 2 (14 + 2) = 60

Mass of carbon = 12

$$\text{Mass percentage of carbon} = \frac{12}{60} \times 100 = 20\%$$

Mass of oxygen = 16

$$\text{Mass percentage of oxygen} = \frac{16}{60} \times 100 = 26.67\%$$

Mass of nitrogen = 2 × 14 = 28

$$\text{Mass percentage of nitrogen} = \frac{28}{60} \times 100 = 46.66\%$$

Mass of H = 4 × 1 = 4

$$\text{Mass percentage of hydrogen} = \frac{4}{60} \times 100 = 6.67\%$$

(*ii*) Copper sulphate, $CuSO_4.5H_2O$

Molar mass of $CuSO_4.5H_2O$ = 63.5 + 32 + 4 × 16 + 5 × 18

= 249.5

Mass of Cu = 63.5

$$\text{Mass percentage of Cu} = \frac{63.5}{249.5} \times 100 = 25.45$$

Mass of S = 32

$$\text{Mass percentage of S} = \frac{32}{249.5} \times 100 = 12.82\%$$

Mass of O = 9 × 16 = 144

$$\text{Mass percentage of O} = \frac{144}{249.5} \times 100 = 57.77\%$$

Mass of H = 10 × 1 = 10

$$\text{Mass percentage of H} = \frac{10}{249.5} \times 100 = 4.01\%$$

Example 56.

Ferric sulphate is used in water and sewage treatment and in removal of suspended impurities. Its empirical formula is $Fe_2(SO_4)_3$. Calculate the mass percentage of iron, sulphur and oxygen in this compound.

Solution: Molar mass of $Fe_2(SO_4)_3$

= 2 × 56 + 3 (32 + 4 × 16)

= 400

Mass of iron = 2 × 56 = 112

$$\text{Mass percentage of iron} = \frac{2 \times 56}{400} \times 100 = 28\%$$

Mass of sulphur = 32 × 3 = 96

$$\text{Mass percentage of sulphur} = \frac{96}{400} \times 100 = 24\%$$

Mass of oxygen = 3 × 64 = 192

$$\text{Mass percentage of oxygen} = \frac{192}{400} \times 100 = 48\%$$

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❑ **Example 57.**

Calculate the percentage of water of crystallisation in the sample of Mohr salt, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$.

Solution: Molar mass of $FeSO_4 \cdot (NH_4)_2SO_4 . 6H_2O$

$= 56 + (32 + 64) + 2\,(14 + 4)$

$+ (32 + 64) + 6\,(2 \times 1 + 16)$

$= 56 + 96 + 36 + 96 + 108 = 392$

Mass of water $= 6 \times 18 = 108$

$$\text{Percentage of water} = \frac{108}{392} \times 100 = 27.55\%$$

$\therefore$ Water of crystallisation = **27.55%**.

Empirical and Molecular Formula

The chemical formula may be of two types :

(*i*) *Empirical formula* and

(*ii*) *Molecular formula.*

Empirical formula.

The formula which gives the simplest whole number ratio of the atoms of various elements present in one molecule of the compound is called **empirical formula.**

For example, empirical formula of hydrogen peroxide is HO. It represents that hydrogen and oxygen (*i.e.,* H : O) are present in the ratio of 1 : 1 in hydrogen peroxide. Similarly, empirical formula of benzene is CH which indicates that atomic ratio of C : H in benzene is 1 : 1.

Molecular formula

The formula which gives the actual number of atoms of various elements present in one molecule of the compound is called **molecular formula.**

For example, the molecular formula of hydrogen peroxide is H_2O_2, because one molecule of hydrogen peroxide contains two atoms of hydrogen and two atoms of oxygen. Similarly, molecular formula of benzene is C_6H_6 which tells that one molecule of benzene contains 6 atoms of carbon and 6 atoms of hydrogen.

Empirical and molecular formulae of some molecules are given below :

Compound	Empirical formula	Molecular formula
Hydrogen peroxide	HO	H_2O_2
Benzene	CH	C_6H_6
Glucose	CH_2O	$C_6H_{12}O_6$
Sucrose	$C_{12}H_{22}O_{11}$	$C_{12}H_{22}O_{11}$
Naphthalene	C_5H_4	$C_{10}H_8$

❑ **Example 58.**

Write the empirical formula of the compounds having the molecular formulae :

(i) C_6H_6 *(ii)* C_6H_{12} *(iii)* H_2O_2 *(iv)* Na_2CO_3 *(v)* B_2H_6 *(vi)* N_2O_4 *(vii)* H_3PO_4 *(viii)* Fe_2O_3 *(ix)* C_2H_2 *(x)* N_2O_5

Solution: Empirical formula gives the simple whole number ratio of atoms in one molecule of the compound.

(*i*) $C_6H_6 = CH$ (*ii*) $C_6H_{12} = CH_2$

(*iii*) $H_2O_2 = HO$ (*iv*) $Na_2CO_3 = Na_2CO_3$

(*v*) $B_2H_6 = BH_3$ (*vi*) $N_2O_4 = NO_2$

(*vii*) $H_3PO_4 = H_3PO_4$ (*viii*) $Fe_2O_3 = Fe_2O_3$

(*ix*) $C_2H_2 = CH$ (*x*) $N_2O_5 = N_2O_5$

Relation between Empirical and Molecular Formulae

Molecular formula and empirical formula are related as

Molecular formula = *n* (Empirical formula)

where *n* is a simple whole number and may have values 1, 2, 3... It is equal to

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

For example, the molecular mass of benzene is 78. The empirical formula of benzene is CH and therefore, its empirical formula mass is 13.

Thus, $$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

$$= \frac{78}{13} = 6$$

Therefore, molecular formula of benzene = 6(CH) = C_6H_6.

It may be noted that in many cases, the value of *n* comes out to be one and, therefore, empirical formula and molecular formula are same in these cases. For example, empirical and molecular formulae are same for $CuSO_4$, NaCl, $K_2Cr_2O_7$, NH_3, etc.

Determination of the Empirical Formula of a Compound

The empirical formula of a compound can be determined from the *percentage composition of different elements and atomic masses of the elements.*

The **various steps** involved in determining the empirical formula are :

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Step I. *Divide the percentage of each element by its atomic mass. This gives the moles of atoms of various elements in the molecule of the compound.*

$$\text{Moles of atoms} = \frac{\text{Percentage of an element}}{\text{Atomic mass of the element}}$$

Step II. *Divide the result obtained in the above step by the smallest value among them to get the simplest ratio of various atoms.*

Step III. *Make the values obtained above to the nearest whole number and multiply, if necessary, by a suitable integer to make the values whole numbers.* This gives the **simplest whole number ratio.**

Step IV. *Write the symbols of the various elements side by side and insert the numerical value at the right hand lower corner of each symbol.* The formula thus obtained represents the empirical formula of the compound.

Steps for Determination of the Molecular Formula of a Compound

Step I. *Determine the empirical formula as described above.*

Step II. *Calculate the empirical formula mass by adding the atomic masses of the atoms in the empirical formula.*

Step III. *Determine the molecular mass by a suitable method.*

Step IV. *Determine the value* of *n as*

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

Change *n* to the nearest whole number.

Step V. *Multiply empirical formula by n to get the molecular formula.*

Molecular formula = n × Empirical formula.

SOLVED EXAMPLES

❑ **Example 59.**

The molecular mass of an organic compound is 78 and its percentage composition is 92.4% C and 7.6% H. Determine the molecular formula of the compound.

Solution: ***Calculation of empirical formula.***

Element	Percentage	Atomic mass	Moles of atoms	Mole ratio or atomic ratio	Simplest whole no. ratio
C	92.4	12.0	$\frac{92.4}{12.0} = 7.7$	$\frac{7.7}{7.6} = 1.01$	1
H	7.6	1	$\frac{7.6}{1} = 7.6$	$\frac{7.6}{7.6} = 1$	1

The simplest whole number ratio of C : H is 1 : 1

∴ The empirical formula of the compound is CH.

Calculation of molecular formula of the compound.

$$\text{Empirical formula mass} = 1 \times 12 + 1 \times 1 = 13$$

$$\text{Molecular mass} = 78$$

$$\therefore \quad n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{78}{13} = 6$$

Thus, molecular formula of the compound = $6 \times (CH) = \mathbf{C_6H_6}$.

❑ **Example 60.**

An organic compound on analysis gave the following percentage composition : C = 57.8%, H = 3.6% and the rest is oxygen. The vapour density of the compound was found to be 83. Find out the molecular formula of the compound.

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Solution: Calculation of empirical formula.

Element	Percentage	Atomic mass	Moles of atoms	Mole ratio or atomic ratio	Simplest whole no. ratio
C	57.8	12	$\frac{57.8}{12} = 4.82$	$\frac{4.82}{2.41} = 2$	4
H	3.6	1	$\frac{3.6}{1} = 3.60$	$\frac{3.60}{2.41} = 1.49$	3
O	100 – (57.8 + 3.6) = 38.6	16	$\frac{38.6}{16} = 2.41$	$\frac{2.41}{2.41} = 1$	2

$\therefore$ Empirical formula = $C_4H_3O_2$

Calculation of molecular formula

Empirical formula mass = $4 \times 12 + 3 \times 1 + 2 \times 16 = 83$

Molecular mass = $2 \times$ V.D. $= 2 \times 83 = 166$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

$$= \frac{166}{83} = 2$$

Molecular formula = n (Empirical formula)

$= 2\,(C_4H_3O_2) = \mathbf{C_8H_6O_4}$.

Example 61.

Four gram of copper chloride on analysis was found to contain 1.890 g of copper (Cu) and 2.110 of chlorine (Cl). What is the empirical formula of copper chloride ?

Solution:

Step I. ***Calculation of percentage of different elements.***

$$\text{Percentage of Cu in copper chloride} = \frac{\text{Wt. of copper}}{\text{Wt. of copper chloride}} \times 100$$

$$= \frac{1.890}{4.000} \times 100 = 47.3$$

$$\text{Percentage of Cl in copper chloride} = \frac{\text{Weight of chlorine}}{\text{Weight of copper chloride}} \times 100$$

$$= \frac{2.110}{4.000} \times 100 = 52.7$$

Step II. ***Calculation of empirical formula.***

Element	Percentage	Atomic mass	Moles of atoms	Mole ratio or atomic ratio	Simplest whole no. ratio
Cu	47.3	63.5	$\frac{47.3}{63.5} = 0.74$	$\frac{0.74}{0.74} = 1$	1
Cl	52.7	35.5	$\frac{52.7}{35.5} = 1.48$	$\frac{1.84}{0.74} = 2$	2

The simplest whole number ratio of various atoms is :

Cu : Cl as 1 : 2

$\therefore$ The empirical formula of the compound is $CuCl_2$.

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Example 62.

A compound contains 4.07 % hydrogen, 24.27% carbon and 71.65% chlorine. Its molecular mass is 98.96. What are its empirical and molecular formulae ? ***N.C.E.R.T.***

Solution: Step I. ***Calculation of empirical formula***

Elements	Percentage composition	At. mass	Moles of atoms	Mole ratio or atomic ratio
C	24.27	12	$\frac{24.27}{12} = 2.02$	$\frac{2.02}{2.02} = 1$
H	4.07	1	$\frac{4.07}{1} = 4.07$	$\frac{4.07}{2.02} = 2$
Cl	71.65	35.5	$\frac{71.65}{35.5} = 2.02$	$\frac{2.02}{2.02} = 1$

$\therefore$ Empirical formula of the compound = CH_2Cl

Step II. ***Calculation of molecular formula***

Empirical formula mass = At. mass of C + 2 × At. mass of H + At. mass of Cl

= 12 + 2 × 1 + 35.5 = 49.5

Molecular mass = 98.96

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{98.96}{49.5} = 2.$$

$\therefore$ Molecular formula = $(CH_2Cl)_2 = \mathbf{C_2H_4Cl_2}$.

Example 63.

Determine the empirical formula of an oxide of iron which has 69.9% iron and 30.1% oxygen by mass. ***N.C.E.R.T.***

Solution: Step I. Calculation of empirical formula

Elements	At. mass	Percentage composition	Moles of atoms	Mole ratio or atomic ratio	Simplest whole number ratio
Fe	56	69.9	$\frac{69.9}{56} = 1.25$	$\frac{1.25}{1.25} = 1$	2
O	16	30.1	$\frac{30.1}{16} = 1.88$	$\frac{1.88}{1.25} = 1.50$	3

Empirical formula : $\mathbf{Fe_2O_3}$.

Example 64.

(a) Butyric acid contains only C, H and O. A 4.24 mg sample of butyric acid is completely burnt. It gives 8.45 mg of carbon dioxide and 3.46 mg of water. What is the mass percentage of each element in butyric acid ?

(b) The molecular mass of butyric acid was determined by experiment to be 88u. What is the molecular formula ?

Solution: (*a*) Calculation of mass percentage of different elements

Percentage of carbon can be calculated as :

$CO_2 \equiv C$

44 mg 12 mg

44 mg of CO_2 contain C = 12 mg

$$8.45 \text{ mg of } CO_2 \text{ contain C} = \frac{12}{44} \times 8.45 \text{ mg}$$

$\therefore$ $$\text{Percentage of C} = \frac{\text{Weight of carbon}}{\text{Weight of compound}} \times 100$$

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$$= \frac{12}{44} \times \frac{8.45}{4.24} \times 100 = 54.3\%$$

Percentage of hydrogen can be calculated as :

$$H_2O \equiv 2H$$
$$18 \text{ mg} \quad 2 \text{ mg}$$
$$18 \text{ mg of } H_2O \text{ contain H} = 2 \text{ mg}$$
$$3.46 \text{ mg of } H_2O \text{ contain H} = \frac{2}{18} \times 3.46 \text{ mg}$$

$$\therefore \quad \text{Percentage of H} = \frac{\text{Weight of hydrogen}}{\text{Weight of compound}} \times 100$$

$$= \frac{2}{18} \times \frac{3.46}{4.24} \times 100 = 9.0\%$$

$$\text{The sum of the percentages of C and H} = 54.3 + 9.0 = 63.3\%$$
$$\therefore \quad \text{Percentage of O} = 100 - 63.3 = 36.7\%$$

(*b*) Calculation of molecular formula

Element	Percentage	Atomic mass	Moles of atoms	Mole ratio or atomic ratio	Simplest whole no. ratio
C	54.3	12.0	$\frac{54.3}{12.0} = 4.52$	$\frac{4.52}{2.29} = 1.97$	2
H	9.0	1.008	$\frac{9.0}{1.008} = 8.93$	$\frac{8.93}{2.29} = 3.90$	4
O	36.7	16.0	$\frac{36.7}{16.0} = 2.29$	$\frac{2.29}{2.29} = 1.00$	1

The simplest whole number ratio of atom is :

$$C : H : O = 2 : 4 : 1$$

$\therefore$ The empirical formula is C_2H_4O

$$\text{Empirical formula mass} = 2 \times 12 + 4 \times 1 + 16$$
$$= 44 \text{ a.m.u.}$$
$$\text{Molecular mass} = 88 \text{ a.m.u.}$$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

$$n = \frac{88}{44} = 2$$

$\therefore$ Molecular formula of butyric acid $2(C_2H_4O)$ = **$C_4H_8O_2$.**

❑ **Example 65.**

A compound on analysis gave the following percentage composition.

Na = 14.31%, S = 9.97%, H = 6.22% and O = 69.5%.

Calculate the molecular formula of the compound on the assumption that all the hydrogens in the compound are present in combination with oxygen as water of crystallisation. The molecular mass of the compound is 322. [At. mass : Na = 23, S = 32, H = 1, O = 16].

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Solution:

Step I. Calculation of empirical formula

Element	Atomic mass	Percentage composition	Moles of atoms	Mole ratio or atomic ratio
Na	23	14.31	$\frac{14.31}{23} = 0.62$	$\frac{0.62}{0.31} = 2$
S	32	9.97	$\frac{9.97}{32} = 0.31$	$\frac{0.31}{0.31} = 1$
H	1	6.22	$\frac{6.22}{1} = 6.22$	$\frac{6.22}{0.31} = 20$
O	16	69.50	$\frac{69.50}{16} = 4.34$	$\frac{4.34}{0.31} = 14$

Empirical formula of the compound is $Na_2SH_{20}O_{14}$.

Step II. Calculation of molecular formula

Empirical formula mass

$= 2 \times$ At. mass of Na + At. mass of S + $20 \times$ At. mass of H + $14 \times$ At. mass of O

$= 2 \times 23 + 1 \times 32 + 20 \times 1 + 14 \times 16 = 322$

Molecular mass = 322

Now, $n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{322}{322} = 1$

Molecular formula = $(Na_2SH_{20}O_{14}) = Na_2SH_{20}O_{14}$

Since all hydrogen atoms are present in combination with oxygen as water therefore, it means that all the 20 hydrogen atoms must be combined with 10 atoms of oxygen to form 10 molecules of water of crystallisation. The remaining 4 oxygen atoms are present with the compound. Thus,

Molecular formula of the compound = $\mathbf{Na_2SO_4.10H_2O}$

❑ Example 66.

A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g of carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (measured at S.T.P.) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula (ii) molar mass of the gas, and (iii) molecular formula.

Solution: $CO_2 \equiv C$

44 g 12 g

$$\text{Mass of carbon} = \frac{12}{44} \times 3.38 = \mathbf{0.92\ g}$$

$H_2O \equiv H_2$

18 g 2 g

$$\text{Mass of hydrogen} = \frac{2}{18} \times 0.690 = \mathbf{0.077}$$

$$\text{Percentage of C} = \frac{0.922}{(0.922 + 0.077)} \times 100 = \mathbf{92.2\%}$$

$$\text{Precentage of H} = \frac{0.077}{(0.922 + 0.077)} \times 100 = \mathbf{7.7\%}$$

***(i)* Calculation of empirical formula**

Element	Percentage of element	Atomic mass	Moles of atoms	Mole ratio
C	92.2	12	$\frac{92.2}{12} = 7.7$	$\frac{7.7}{7.7} = 1$
H	7.77	1	$\frac{7.77}{1} = 7.7$	$\frac{7.7}{7.7} = 1$

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Empirical formula = CH

***(ii)* Calculation of molar mass**

10.0 L of gas at S.T.P. weigh = 11.6 g

22.4 L of gas at S.T.P. weigh = $\frac{11.6}{10.0} \times 22.4$

= **26 g mol^{-1}.**

***(iii)* Calculation of molecular formula**

Empirical formula mass = 12 + 1 = 13

Molecular mass = 26

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

$$= \frac{26}{13} = \mathbf{2}$$

$\therefore$ Molecular formula = 2 (CH)

= **C_2H_2**

Example 67.

A crystalline salt on being rendered anhydrous loses 45.6% of its weight. The composition of anhydrous salt is : Al = 10.5%, K = 15.1%, S = 24.8% and O = 49.6%. Calculate the formula of anhydrous salt and crystalline salt (At. mass of Al = 27, K = 39, S = 32, O = 16).

Solution:

Step I. Calculation of empirical formula

Element	Percentage of element	Atomic mass	Moles of atoms	Mole ratio	Simplest whole no. ratio
K	15.1	39	$\frac{15.1}{39} = 0.38$	$\frac{0.38}{0.38} = 1$	1
Al	10.5	27	$\frac{10.5}{27} = 0.38$	$\frac{0.38}{0.38} = 1$	1
S	24.8	32	$\frac{24.8}{32} = 0.775$	$\frac{0.775}{0.38} = 2.04$	2
O	49.6	16	$\frac{49.6}{16} = 3.1$	$\frac{3.1}{0.38} = 8.1$	8

The simplest atomic ratio of K : Al : S : O is 1 : 1: 2 : 8. The empirical formula of the anhydrous salt is : $KAlS_2O_8$.

Step II. ***To calculate the empirical formula mass of anhydrous salt.***

Empirical formula mass of anhydrous salt

= 39 + 27 + 64 + 128 = 258.

Step III. ***To calculate the amount of water associated with 258 parts by weight of compound.***

Let the weight of hydrated salt be 100 g

$\therefore$ The weight of water lost = 45.6 g

$\therefore$ The weight of anhydrous salt = 100 – 45.6 g

= 54.4 g

If the weight of anhydrous salt is 54.4 gm, the weight of water in the crystalline salt = 45.6 gm.

If the weight of anhydrous salt in 258 gm, the weight of water in the crystalline salt

$$= \frac{45.6}{54.4} \times 258 = 216.2 \text{ g}$$

Step IV. ***To calculate the number of molecules of water of crystallisation.***

It is clear from the above calculations that 216.2 parts by weight of water are present in combination with 258 parts be weight of the salt.

$\therefore$ The number of molecules of water of crystallisation corresponding to 216.2 parts by weight of water

$$= \frac{216.2}{18} = 12$$

$\therefore$ The simplest formula of crystalline salt is **$KAlS_2O_8.12H_2O$.**

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Practice Problems

50. (*i*) Calculate the mass percentage of various elements present in magnesium sulphate, $MgSO_4$.
(*ii*) Calculate the percentage of cation in ammonium dichromate.

51. An organic compound containing carbon, hydrogen and oxygen gave the following percentage composition :
C = 40.68%, H = 5.08%
The vapour density of the compound is 59. Calculate the molecular formula of the compound.

52. (*i*) The elemental composition of butyric acid was found to be 54.2% C, 9.2% H and 36.6% O. Determine its empirical formula.
(*ii*) The molecular mass of butyric acid was determined by an experiment to be 88 u. What is its molecular formula ?

53. An oxide of nitrogen contains 30.43% of nitrogen. The molecular weight of the compound is equal to 92 a.m.u. Calculate the molecular formula of the compound.

54. Calculate the empirical and molecular formula of the compound having the following percentage composition :
Na = 36.5%, H = 0.8%, P = 24.6%, O = 38.1%
The molecular mass of the compound is 126 a.m.u. Also name the compound.

55. A crystalline salt when heated becomes anhydrous and loses 51.2% of its weight. The anhydrous salt on analysis gave the following percentage composition :
Mg = 20.0%, S = 26.66%, O = 53.33%
Calculate the molecular formula of the anhydrous salt and the crystalline salt. Molecular weight of the anhydrous salt is 120.

56. Calculate the empirical formula of a mineral which has the following percentage composition :
CuO = 44.82%, SiO_2 = 34.83% and water = 20.35%
(at. wt. of Cu = 63.5, Si = 28).

57. Determine the empirical formula of a compound having percentage composition as :
Iron = 20% ; sulphur = 11.5% ; oxygen = 23.1% and water molecules = 45.4%
(At. mass of Fe = 56, S = 32)

* **Hint.** Treat water molecules as one entity.

Answers to Practice Problems

50. (*i*) Mg = 20 %, S = 26.67 %, O = 53.33 %
(*ii*) 14.29%

51. $C_4H_6O_4$

52. (*i*) C_2H_4O (*ii*) $C_4H_8O_2$

53. N_2O_4

54. The empirical and molecular formula is, Na_2HPO_3, sodium hydrogen phosphite.

55. $MgSO_4 . 7H_2O$

56. $CuO . SiO_2 . 2H_2O$

57. $FeSO_4 . 7H_2O$

Hints & Solutions on page 79

STOICHIOMETRY OF CHEMICAL REACTIONS

The term *stoichiometry means the quantitative relationships among the reactants and the products in a reaction.* Stoichiometry is derived from the Greek words *stoicheion* meaning element and *metron* meaning measure. It is based on the fact that *the stoichiometric coefficients in a chemical equation can be interpreted as the number of moles of each substance (reactants or products).* For example, consider the reaction between nitrogen and hydrogen to form ammonia as :

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

The stoichiometric coefficients in the equation indicate that 1 molecule of nitrogen combines with 3 molecules of hydrogen to form 2 molecules of ammonia.

$$\underset{\text{1 molecule}}{N_2(g)} + \underset{\text{3 molecules}}{3H_2(g)} \longrightarrow \underset{\text{2 molecules}}{2NH_3(g)}$$

Multiplying by 6.022×10^{23} the entire equation, we get

$$\underset{\text{molecules}}{1 \times 6.022 \times 10^{23}} \quad \underset{\text{molecules}}{3 \times 6.022 \times 10^{23}} \quad \underset{\text{molecules}}{2 \times 6.022 \times 10^{23}}$$

This means

1 mol 3 mol 2 mol

Taking molar masses into consideration

28.0 g $3 \times 2 = 6.0$ g $2 \times 17 = 34$ g

The interpretation of the coefficients as the number of moles is the basis of all stoichiometric calculations.

Thus, to carry out stoichiometric calculations, the first step is writing the chemical equation for the reaction and then balancing it. The balanced chemical equation gives the stoichiometric coefficients which give the proportion by moles.

Chemical Equations

A chemical equation is a statement of a chemical reaction in terms of the symbols and formulae of the species involved in the reaction. The **chemical equation** may be defined as :

a brief representation of a chemical change in terms of symbols and formulae of substances involved in it.

For example, the reaction of silver nitrate with sodium chloride to give silver chloride and sodium nitrate may be represented as

$$\underbrace{AgNO_3 + NaCl}_{\text{Reactants}} \longrightarrow \underbrace{AgCl + NaNO_3}_{\text{Products}}$$

The substances which react among themselves to bring about the chemical changes are known as **reactants** whereas, the substances which are produced as a result of the chemical change, are known as **products.**

Essentials of Chemical Equation

A chemical equation must fulfil the following conditions :

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(*i*) *It must be consistent with the experimental facts. i.e.,* a chemical equation must represent a true chemical change. If a chemical reaction is not possible between certain substances it cannot be represented by a chemical equation.

(*ii*) *It should be balanced i.e.,* the total number of atoms an both sides of the equation must be equal.

(*iii*) *It should be molecular i.e.,* the elementary gases like hydrogen, oxygen, nitrogen, etc. must be represented in molecular form as H_2, O_2, N_2, etc.

Information Conveyed by a Chemical Equation

A chemical equation conveys both qualitative and quantitative informations.

Qualitatively, *a chemical equation tells the names of the various reactants and the products.*

Quantitatively, *a chemical equation represents :*

(*i*) the relative number of reactant and product species (atoms or molecules) taking part in the reaction.

(*ii*) *the relative number of moles of the reactants and products.*

(*iii*) *the relative masses of the reactants and products.*

(*iv*) *the relative volumes of gaseous reactants and products.*

Thus, the chemical equation for the reaction :

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O\ (g)$

gives the following information :

(*i*) **One molecule** of $CH_4(g)$ reacts with **2 molecules** of $O_2(g)$ to give **one molecule** of $CO_2(g)$ and **2 molecules** of $H_2O(g)$.

(*ii*) **One mole** of $CH_4(g)$ reacts with **2 moles** of $O_2(g)$ to give **one mole** of $CO_2(g)$ and **2 moles** of $H_2O(g)$.

(*iii*) **16 *g*** of $CH_4(g)$ reacts with **2 × 32 *g*** of $O_2(g)$ to give **44 *g*** of CO_2 and **2 × 18 *g*** of $H_2O(g)$.

(*iv*) **22.4 L** of $CH_4(g)$ reacts with **44.8 L** of $O_2(g)$ to give **22.4 L** of CO_2 and **44.8 L** of $H_2O(g)$ at N.T.P.

Limitations of Chemical Equations and Methods to make them more Informative

The chemical equations, as such do not give us the following informations :

(*i*) The physical states of the reactants and products.

(*ii*) The concentration of the reactants and products.

(*iii*) The conditions such as temperature, pressure or catalyst, etc. which affect the reaction.

(*iv*) The heat changes accompanying the reaction *i.e.,* whether heat is evolved or absorbed during the reaction.

(*v*) The formation of a precipitate or the evolution of gas in the reaction.

(*vi*) The speed of the reaction.

(*vii*) The nature of the reaction *i.e.,* whether the chemical reaction is reversible or irreversible.

Removal of Drawbacks of Chemical Equations

The chemical equation can be made more informative by the following modifications;

(*a*) *The physical states of the reactants and products can be specified.* For this, we use *s* (for solids), *l* (for liquids) and *g* (for gases). Sometimes, the letter *aq* is given to represent that the given substance has been dissolved in excess of water. For example,

$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2\ (aq) + H_2(g)$

(*b*) In order to express the strength of acid or base used in the reaction, the words *conc.* for concentrated and *dil.* for dilute are used before the formula of the acid or base. For example,

$Zn\ (s) + \text{dil. } 2HCl\ (aq) \longrightarrow ZnCl_2(aq) + H_2(g)$

(*c*) *The conditions of the reaction such as temperature, pressure, catalyst, etc.* may be written on the arrow between the reactants and products. For example,

$$N_2(g) + 3H_2(g) \xrightarrow[600\ \text{atm.}]{\text{Fe/Mo, 723 K}} 2NH_3\ (g)$$

The above equation indicates that the reaction between hydrogen and nitrogen has been carried out in the presence of Fe/Mo (catalyst) at 723 K and 600 atm. pressure.

(*d*) *Heat changes taking place during the reaction may be expressed in the equation.* For example,

$C(s) + O_2\ (g) \longrightarrow CO_2(g) + 394\ \text{kJ}$ (Heat is evoled)

$N_2(g) + O_2(g) \longrightarrow 2NO\ (g) - 180.5\ \text{kJ}$ (Heat is a absorbed)

(*e*) *The formation of a precipitate, if any, in a reaction can be expressed by writing the word ppt. or by an arrow pointing downward.* For example,

$$AgNO_3(aq) + NaCl(aq) \longrightarrow \underset{\text{(ppt)}}{AgCl(s)\downarrow} + NaNO_3(aq)$$

Similarly, the evolution of a gas in a chemical reaction can be indicated by an arrow pointing upward. For example,

$Zn(s) + 2HCl\ (aq) \longrightarrow ZnCl_2(aq) + H_2(g)\uparrow$

(*f*) The distinction between slow and fast reactions can be made by writing word *slow* and *fast* on the arrow head.

(*g*) The reversible nature of the reaction maybe indicated by double headed arrow which indicates that the reaction is occurring in the forward as well as in the backward direction :

$$N_2(g) + 3H_2\ (g) \underset{\text{Backward}}{\overset{\text{Forward}}{\rightleftharpoons}} 2NH_3\ (g)$$

Balancing of Chemical Equation

A correct chemical equation must be in accordance with the law of conservation of mass according to which the total mass of the reactants must be equal to the total mass of the products. In other words, the number of atoms of each kind in the reactants must be equal to the number of atoms of same kind in the products. *Such a chemical equation which has an equal number of atoms of each element in the reactants and the products is called* **balanced chemical equation.** For example, the reaction between hydrogen and oxygen to form water may be written as

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$$H_2 + O_2 \longrightarrow H_2O$$

But this equation has two atoms of O on the reactants side but only one atom of O on the products side. Therefore, it does not obey law of conservation of mass. By choosing suitable coefficients, the equation may be balanced as :

$$2H_2 + O_2 \longrightarrow 2H_2O$$

The balancing of a chemical equation means to equalise the number of atoms of each element on both sides of the equation. There are many methods to balance a chemical equation. Some of these methods are :

(*i*) Hit and Trial method or Trial and Error method.

(*ii*) Partial equation method

(*iii*) Oxidation number method

(*iv*) Ion-electron method.

The first two methods are discussed below while the other two methods will be taken up in Unit 8 (Redox reactions).

Hit and Trial Method or Trial and Error method

This method involves the following steps :

(*i*) *Write the symbols and formulae of the reactants and the products in the form of a skeleton equation.*

(*ii*) *If any elementary gas appears, change it to its atomic state.*

(*iii*) *Select the formula containing maximum number of atoms and start the process of balancing.*

(*iv*) *In case, the above method fails, then start balancing the atoms which appear minimum number of times.*

(*v*) *Atoms of elementary gases are balanced last of all.*

(*vi*) *Once all the atoms are balanced, change the equation into the molecular form.*

(*vii*) *Verify that the number of atoms of each element is balanced in the final equation.*

For example, let us consider the equation :

$$Fe + H_2O \longrightarrow Fe_3O_4 + H_2$$

(*i*) Changing the elementary substance hydrogen to atomic form,

$$Fe + H_2O \longrightarrow Fe_3O_4 + 2H$$

(*ii*) Fe_3O_4 has largest number of atoms. To balance this, multiply H_2O by 4 to balance oxygen atoms. In 4 molecules of H_2O, there are 8 atoms of H which are balanced by multiplying H on the R.H.S by 8.

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 8\,H$$

(*iii*) Converting to molecular form,

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$$

is a balanced equation.

Similarly, some other balanced equations are :

$$4Fe\,(s) + 3O_2\,(g) \longrightarrow 2Fe_2O_3\,(s)$$
$$P_4\,(s) + 5O_2\,(g) \longrightarrow P_4O_{10}\,(s)$$
$$2Mg\,(s) + O_2\,(g) \longrightarrow 2MgO\,(s)$$

SOLVED EXAMPLES

Example 68.

Balance the equation

$$C_3H_8 + O_2 \longrightarrow CO_2 + H_2O$$

Solution: Converting the oxygen to elementary state

$$C_3H_8 + O \longrightarrow CO_2 + H_2O$$

unbalanced equation

Balancing carbon atoms

$$C_3H_8 + O \longrightarrow 3CO_2 + H_2O$$

Balancing hydrogen atoms

$$C_3H_8 + O \longrightarrow 3CO_2 + 4H_2O$$

Balancing oxygen atoms

$$C_3H_8 + 10\,O \longrightarrow 3CO_2 + 4H_2O$$

Changing to molecular form

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

Example 69.

Balance the following skeleton equation :

$$As_2O_3 + SnCl_2 + HCl \longrightarrow SnCl_4 + As + H_2O$$

Solution: The skeleton equation is :

$$As_2O_3 + SnCl_2 + HCl \longrightarrow SnCl_4 + As + H_2O$$

Balancing arsenic and oxygen atoms by multiplying As by 2 and H_2O by 3

$$As_2O_3 + SnCl_2 + HCl \longrightarrow SnCl_4 + 2As + 3H_2O$$

Multiply HCl by 6 to balance H atoms

$$As_2O_3 + SnCl_2 + 6HCl \longrightarrow SnCl_4 + 2As + 3H_2O$$

To balance chlorine atoms, multiply $SnCl_2$ and $SnCl_4$ both by 3.

$$As_2O_3 + 3SnCl_2 + 6HCl \longrightarrow 3SnCl_4 + 2As + 3H_2O$$

Partial Equation Method

This is a better method than the hit and trial method. It involves the following steps :

(*i*) *The given chemical reaction is supposed to occur* in steps and chemical equation called **partial equation,** is written for each step.

(*ii*) *Each partial equation is balanced separately by hit and trial method as discussed earlier.*

(*iii*) *The partial equations are multiplied by suitable numbers if necessary, so as to cancel out the species which are not involved in the original reactants and the final products.*

(*iv*) *Finally, the partial equations are added to get the final equation.*

Let us illustrate this method with an example of reaction between copper and nitric acid. The reaction is written as :

$$Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + N_2O + H_2O$$

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(*i*) The probable partial equations for the above reaction are :

$$Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + 2H$$
$$HNO_3 + H \longrightarrow N_2O + H_2O$$

(*ii*) Balance the partial chemical equations separately by hit and trial method as

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H$$
$$2HNO_3 + 8H \longrightarrow N_2O + 5H_2O$$

(*iii*) Multiply the first partial equation by 4 in order to cancel out H atoms in the two equations since they do not appear in the final equation. Finally add the two equations

$$[Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H] \times 4$$
$$2HNO_3 + 8H \longrightarrow N_2O + 5H_2O$$

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

Practice Problems

58. Balance the following equations by hit and trial method :

(*a*) $KMnO_4 + HCl \longrightarrow KCl + MnCl_2 + H_2O + Cl_2$

(*b*) $H_2S + SO_2 \longrightarrow S + H_2O$

(*c*) $K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O + O_2$

(*d*) $KMnO_4 + KOH \longrightarrow K_2MnO_4 + O_2 + H_2O$

(*e*) $Mg_3N_2 + H_2O \longrightarrow Mg(OH)_2 + NH_3$

(*f*) $Al_4C_3 + H_2O \longrightarrow Al(OH)_3 + CH_4$

(*g*) $FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$

(*h*) $KMnO_4 + H_2S + H_2SO_4 \longrightarrow KHSO_4 + MnSO_4 + S + H_2O$

(*i*) $C_3H_8(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$

59. Balance the following equations by partial equation method :

(*i*) $NaOH + Cl_2 \longrightarrow NaCl + NaClO_3 + H_2O$

(*ii*) $H_2S + HNO_3 \longrightarrow NO + H_2O + S$

(*iii*) $C + H_2SO_4 \longrightarrow CO_2 + SO_2 + H_2O$

(*iv*) $I_2 + HNO_3 \longrightarrow NO_2 + HIO_3 + H_2O$

(*v*) $P_4 + HNO_3 \longrightarrow H_3PO_4 + NO_2 + H_2O$

Answers to Practice Problems

58. (*a*) $2KMnO_4 + 16\,HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

(*b*) $2H_2S + SO_2 \longrightarrow 2H_2O + 3S$

(*c*) $2K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$

(*d*) $4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + O_2 + 2H_2O$

(*e*) $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

(*f*) $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$

(*g*) $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

(*h*) $2KMnO_4 + 5H_2S + 4H_2SO_4 \longrightarrow 2KHSO_4 + 2MnSO_4 + 5S + 8H_2O$

(*i*) $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$

59. (*i*) $6NaOH + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

(*ii*) $3H_2S + 2HNO_3 \longrightarrow 2NO + 4H_2O + 3S$

(*iii*) $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$

(*iv*) $I_2 + 10HNO_3 \longrightarrow 10NO_2 + 2HIO_3 + 4H_2O$

(*v*) $P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 4H_2O + 20NO_2$

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STOICHIOMETRIC CALCULATIONS

Problems Based on Chemical Equations (Stoichiometry)

Solving of stoichiometric problems is very important. It requires grasp and application of mole concept, balancing of chemical equations and care in the conversion of units.

The problems based upon chemical equations may be classified as :

(*i*) **Mole to mole relationships.** In these problems, the moles of one of the reactants/products is to be calculated if that of other reactants/products are given.

(*ii*) **Mass-mass relationships.** In these problems, the mass of one of the reactants/products is to be calculated if that of the other reactants/products are given.

(*iii*) **Mass-volume relationship.** In these problems, mass or volume of one of the reactants or products is calculated from the mass or volume of other substances.

(*iv*) **Volume-volume relationship.** In these problems, the volume of one of the reactants/products is given and that of the other is to be calculated.

The **main steps** for solving such problems are :

(i) Write down the balanced chemical equation.

(ii) Write down the moles or gram atomic or gram molecular masses of the substances whose quantitites are given or have to be calculated. In case, there are two or more atoms or molecules of a substance, multiply the mole or gram atomic mass or molecular mass by the number of atoms or molecules.

(iii) Write down the actual quantities of the substances given. For the substances whose weights/volumes have to be calculated, write the sign of interrogation (?)

(iv) Calculate the result by a unitary method.

This method can be illustrated by the following examples :

SOLVED EXAMPLES

Type I. Mole to mole relationship

❑ Example 70.

How many moles of nitrogen are needed to produce 8.2 moles of ammonia by reaction with hydrogen ?

Solution: The balanced chemical equation is :

$$\underset{?}{N_2} + 3H_2 \longrightarrow \underset{8.2\ mol}{2NH_3}$$

2 mol of NH_3 are produced from = 1 mol of N_2

8.2 mol of NH_3 are produced from = $\frac{1}{2} \times 8.2$

= **4.1 mol of N_2**

❑ Example 71.

How many moles of iron can be made from Fe_2O_3 by the use of 16 mol of carbon monoxide in the following reaction :

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

Solution: The balanced equation is :

$$Fe_2O_3 + \underset{16\ mol}{3CO} \longrightarrow \underset{?}{2Fe} + 3CO_2$$

3 mol of CO are used to make = 2 mol Fe

16 mol of CO are used to make = $\frac{2}{3} \times 16$

= **10.67 mol**

Type II. Mass to mass or Mole to mass relationship

❑ Example 72.

Calculate the amount of water in grams produced by combustion of 16 g methane (CH_4). ***N.C.E.R.T.***

Solution: The balanced chemical equation is

$$\underset{\substack{1\ mol \\ 16\ g \\ 16\ g}}{CH_4(g)} + 2O_2(g) \longrightarrow CO_2(g) + \underset{\substack{2\ mol \\ 36\ g \\ ?}}{2H_2O(g)}$$

From the equation, it is clear that 16 g of methane produces 36 g of water.

❑ Example 73.

How many moles of methane are required to produce 22g of $CO_2(g)$ after combustions ?

N.C.E.R.T.

Solution: The balanced equation is

$$\underset{1\ mol}{CH_4(g)} + 2O_2(g) \longrightarrow \underset{\substack{1\ mol \\ 44\ g \\ 22\ g}}{CO_2(g)} + 2H_2O(g)$$

44 g of CO_2 (g) are produced from = 1 mol of CH_4

22 g of CO_2 g will be produced by burning CH_4 = $\frac{1 \times 22}{44}$

= **0.5 mol.**

❑ Example 74.

Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid (HCl) according to the reaction :

$$MnO_2(s) + 4HCl(aq) \longrightarrow MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$$

How many grams of HCl react with 5.0 g of manganese dioxide ? ***N.C.E.R.T.***

Solution: The balanced chemical equation is :

$$MnO_2(s) + 4HCl(aq) \longrightarrow MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$$

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1 mol 4 mol
55 + 2 × 16 4 × (1 + 35.5)
= 87 g = 146.0 g
5 g ?

87 g of MnO_2 react with 146.0 g of HCl

5 g of MnO_2 will react with = $\frac{146.0}{86} \times 5$

= **8.39 g**

❑ Example 75.

What mass of calcium oxide will be obtained by heating 3 mol of $CaCO_3$?

Solution: The balanced chemical equation is :

$CaCO_3 \longrightarrow CaO + CO_2$
1 mol 1 mol
40 + 16
= 56
3 mol ?

1 mol of $CaCO_3$ on heating gives CaO = 56 g
3 mol of $CaCO_3$ on heating gives CaO = 56 × 3

= 168 g

❑ Example 76.

Oxygen is prepared by the catalytic decomposition of potassium chlorate ($KClO_3$). Decomposition of potassium chlorate gives potassium chloride (KCl) and oxygen (O_2). If 2.4 mol of oxygen is needed for an experiment, how many grams of potassium chlorate must be decomposed ?

Solution: The balanced equation is

$2\,KClO_3\,(s) \longrightarrow 2KCl(s) + 3O_2(g)$
2 mol 3 mol
2 × (30 + 35.5 + 3 × 16)
= 245 g
? 2.4 mol

3 mol of O_2 is produced by decomposition of $KClO_3$ = 245 g

2.4 mol of O_2 will be produced by the decomposition of

$KClO_3 = \frac{245 \times 2.4}{3}$ **= 196.0 g**

❑ Example 77.

Calculate the weight of iron which will be converted into its oxide (Fe_3O_4) by the action of 14.4 g of steam on it.

Solution: The balanced chemical equation is:

$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$
3 mol 4 mol
3 × 56 4 × 18
= 168 g = 72 g

Now 72 g of steam react with = 168 g of Fe

14.4 g of steam will react with = $\frac{168}{72} \times 14.4$

= 33.6 g

❑ Example 78.

How many grams of chlorine are required to completely react with 0.40 g of hydrogen (H_2) to yield hydrochloric acid (HCl) ? Also calculate the amount of HCl formed.

Solution: The balanced chemical equation is :

$H_2 + Cl_2 \longrightarrow 2HCl$
1 mol 1 mol
2 g 2 × 35.5 = 71 g
2 g of H_2 react with = 71 g Cl_2

0.40 g of H_2 would react with = $\frac{71}{2} \times 0.4$ = **14.2 g Cl_2**

Now,

$H_2 + Cl_2 \longrightarrow 2HCl$
1 mol 2 mol
2 g 73 g
2 g of hydrogen give HCl = 73 g

0.40 g of hydrogen will give HCl = $\frac{73}{2} \times 0.40$ = **14.6 g**

❑ Example 79.

What weight of zinc would be required to produce enough hydrogen to reduce completely 8.5 g of copper oxide to copper ?

Solution: (*i*) **Calculation of H_2 required to reduce CuO to Cu.**

$CuO + H_2 \longrightarrow Cu + H_2O$
1 mol 1 mol
63.5 + 16 = 79.5 g 2 g

One mole of CuO require 1 mole of H_2 for reduction to copper

or 79.5 g of CuO require H_2 for reduction to copper = 2 g

8.5 g of CuO require H_2 for reduction to copper = $\frac{2}{79.5} \times 8.5$

= 0.214 g

(*ii*) **Calculation of weight of zinc required to produce H_2**

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$
1 mol 1 mol
65 g 2 g
? 0.214 g

2 g of H_2 is produced from zinc = 65 g

0.214 g of H_2 would be produced from zinc = $\frac{65}{2} \times 0.214$

= 6.955 g

❑ Example 80.

Calculate the amount of lime $Ca(OH)_2$ required to remove the hardness of 60,000 litres of well water containing 16.2 g of calcium bicarbonate per hundred litre. (Atomic masses Ca = 40, C = 12, O = 16, H = 1)

Solution: (*i*) **Calculation of the weight of calcium bicarbonate present.**

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Wt. of calcium bicarbonate present in 100 litres of well water = 16.2 g

Wt. of calcium bicarbonate present in 60,000 litres of well water = $\frac{16.2}{100} \times 60000$ g = 9720 g

(*ii*) *Calculation of the quantity of lime required.*

The equation involved is :

$$\underset{\substack{40+2+24+96\\=162\\162}}{Ca(HCO_3)_2} + \underset{\substack{40+32+2\\=74\\?}}{Ca(OH)_2} \longrightarrow 2CaCO_3 + 2H_2O$$

∴ One mole of calcium bicarbonate requires one mole of calcium hydroxide

or 162 g of $Ca(HCO_3)_2$ require = 74 g of $Ca(OH)_2$

∴ 9720 g of $Ca(HCO_3)_2$ will require = $\frac{74}{162} \times 9720$ g of $Ca(OH)_2$

= 4440 g of $Ca(OH)_2$

Hence the quantity of lime required = **4440 g = 4.44 kg**

❑ Example 81.

A 1.84 g mixture of calcium carbonate and magnesium carbonate upon heating gave 0.96 g residue. Calculate the percentage composition of the mixture (At. mass of Ca = 40, Mg = 24, C = 12 and O = 16).

Solution: Calcium carbonate and magnesium carbonate on heating give CaO and MgO as residues.

$$\underset{100\text{ g}}{CaCO_3} \xrightarrow{\text{heat}} \underset{56\text{ g}}{CaO} + CO_2$$

$$\underset{84\text{ g}}{MgCO_3} \xrightarrow{\text{heat}} \underset{40\text{ g}}{MgO} + CO_2$$

Let $CaCO_3$ present in the mixture = x g

Wt. of $MgCO_3$ in the mixture = $(1.84 - x)$ g

Now, 100 g of $CaCO_3$ give CaO = 56 g

x g of $CaCO_3$ give CaO = $\frac{56}{100} \times x$ g

Similarly, 84 g of $MgCO_3$ give MgO = 40 g

$(1.84 - x)$ g of $MgCO_3$ give MgO = $\frac{40}{84} \times (1.84 - x)$

Total residue obtained,

$$\frac{56x}{100} + \frac{40}{84}(1.84 - x) = 0.96$$

$$4704\,x + 7360 - 4000\,x = 8064$$

$$704\,x = 704$$

$$x = \frac{704}{704} = 1 \text{ g}$$

Weight of $CaCO_3$ in the mixture = 1 g

Weight of $MgCO_3$ in the mixture = 1.84 – 1 = 0.84 g

$$\% \text{ of } CaCO_3 = \frac{1}{1.84} \times 100 = \mathbf{54.35\%}$$

$$\% \text{ of } MgCO_3 = \frac{0.84}{1.84} \times 100 = \mathbf{45.65\%}$$

Type III. Mass – Volume relationship

❑ Example 82.

An impure sample of sodium chloride which weighed 1.20 g gave on treatment with excess of $AgNO_3$ solution 2.40 g of silver chloride as a precipitate. Calculate the percentage purity of the sample.

Solution:

$$\underset{\substack{23+35.5\\=58.5\\?}}{NaCl} + AgNO_3 \longrightarrow \underset{\substack{108+35.5\\=143.5\\2.40\text{ g}}}{AgCl} + NaNO_3$$

143.5 g of AgCl is obtained from 58.5 g of pure NaCl

2.40 g of AgCl is obtained from pure NaCl

$$= \frac{58.5}{143.5} \times 2.40 = 0.978 \text{ g}$$

Now, 1.20 g of NaCl contain pure NaCl = 0.978 g

100 g of NaCl contain pure NaCl = $\frac{0.978}{1.20} \times 100 = 81.5$ g

Percentage purity of sample = **81.5%**

❑ Example 83.

A 2.0 g of sample containing Na_2CO and $NaHCO_3$ loses 0.248 g when heated to 300°C, the temperature at which $NaHCO_3$ decomposes to Na_2CO_3, CO_2 and water. What is the percentage of Na_2CO_3 in the mixture ?

Solution: The balanced chemical equation is :

$$\underset{2(23+1+12+48)\\=168}{2NaHCO_3} \longrightarrow Na_2CO_3 + \underset{18\text{ g}}{H_2O} + \underset{44\text{ g}}{CO_2}$$

CO_2 and H_2O will escape as gases at 300°C. Therefore, loss in weight would correspond to the weight of H_2O and CO_2.

Total mass of CO_2 + water lost by heating 168 g of $NaHCO_3$ = (18 + 44) = 62 g

62 g of weight is lost by heating $NaHCO_3$ = 168 g

0.248 g of weight is lost by heating $NaHCO_3$

$$= \frac{168}{62} \times 0.248 = 0.672$$

2 g sample contain $NaHCO_3$ = 0.672 g

Weight of Na_2CO_3 in sample = 2 × 0.672 = 1.328 g

∴ Percentage of Na_2CO_3 = $\frac{1.328}{2} \times 100 = \mathbf{66.4\%}$

The equations involving volume are based upon the fact that 1 mol of all gases at N.T.P. occupy 22.4 L. The problems involving different conditions of temperature and pressure are described in next unit.

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❑ Example 84.

Calculate the amount of $KClO_3$ needed to supply sufficient oxygen for burning 112 L of CO gas at N.T.P.

Solution: Calclation of O_2 gas required to burn 112 L of CO.

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2$$

1 mol 0.5 mol

22.4 L at N.T.P.

22.4 L of CO at N.T.P. require O_2 = 0.5 mol

112 L of CO at N.T.P. require $O_2 = \frac{0.5}{22.4} \times 112$

$= 2.5$ mol

This O_2 is to be obtained by heating $KClO_3$.

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

2 mol 3 mol

$2(39 + 35.5 + 3 \times 16) = 245$ g

3 mol of O_2 is produced from $KClO_3$ = 245 g

2.5 mol of O_2 is produced from $KClO_3 = \frac{245 \times 25}{3}$

$=$ **204.167 g**

❑ Example 85.

What volume of air at N.T.P. containing 21% of oxygen by volume is required to completely burn 1000 g of sulphur containing 4% incombustible matter ?

Solution: The balanced chemical equation is :

$$S + O_2 \longrightarrow SO_2$$

1 mol 1 mol

32 g 22.4 L

Amount of sulphur in the sample

$$= \frac{1000 \times 96}{100} = 960 \text{ g}$$

32 g of sulphur require oxygen at N.T.P. = 22.4 L

960 g of sulphur require oxygen at N.T.P.

$$= \frac{22.4}{32} \times 960$$

$= 672$ L

Volume of air required $= \frac{672 \times 100}{21}$

$=$ **3200 L**

Type IV. Volume - Volume relationship

❑ Example 86.

Calculate the volume of oxygen at N.T.P. that would be required to convert 5.2 L of carbon monoxide to carbon dioxide.

Solution: The balanced chemical equation is :

$$2CO + O_2 \longrightarrow 2CO_2$$

2 mol 1 mol

2×22.4 L 22.4 L

Volume of oxygen required to convert 2×22.4 L of CO at N.T.P. = 22.4 L

Volume of oxygen required to convert 5.2 L of CO at N.T.P. $= \frac{22.4}{2 \times 22.4} \times 5.2$

$=$ **2.6 L**

❑ Example 87.

What volume of oxygen at S.T.P. is required to effect complete combustion of 200 cm^3 of acetylene and what would be the volume of carbon dioxide formed ?

Solution: The balanced chemical equation is :

$$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$$

2 mol 5 mol 4 mol

2×22400 cm^3 5×22400 cm^3 4×22400 cm^3

(*i*) **Calculation of volume of O_2 at S.T.P. required to effect complete combustion of 200 cm^3 of acetylene.**

2×22400 cm^3 of acetylene require O_2 for complete combustion = 5×22400 cm^3

200 cm^3 of acetylene require O_2 for complete combustion $= \frac{5 \times 22400}{2 \times 22400} \times 200$

$=$ **500 cm^3 at S.T.P**

(*ii*) **Calculation of volume of carbon dioxide formed**

2×22400 cm^3 of acetylene produce CO_2

$= 4 \times 22400$

$\therefore$ 200 cm^3 of acetylene produce CO_2

$= \frac{4 \times 22400}{2 \times 22400} \times 200$

$=$ **400 cm^3 at S.T.P.**

Practice Problems

60. How much iron can be obtained by the reduction of 1 kg of Fe_2O_3 ?

61. An hourly energy requirement of an astronaut can be satisfied by the energy released when 34 grams of sucrose ($C_{12}H_{22}O_{11}$) are burnt in his body. How many grams of oxygen would he need to be carried in space capsule to meet his requirement for one day ?

62. How much marble of 96.5% purity would be required to prepare 100 litres of carbon dioxide at S.T.P. when marble is acted upon by dil HCl ?

63. 5.6 litres of methane gas (CH_4) is ignited in oxygen gas. Calculate the number of moles of CO_2 formed.

64. Calculate the percentage yield of the reaction if 64 g $NaBH_4$ with iodine produced 15.0 g of BI_3.

$NaBH_4 + 4I_2 \longrightarrow BI_3 + NaI + 4HI$

(At. mass, Na = 23, B = 10.8, I = 127)

65. NO_2^- ion in KNO_2 is oxidised to NO_3^- ion by the action of $KMnO_4$ in H_2SO_4 solution according to the reaction :

$5KNO_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 5KNO_3 + 2MnSO_4 + 5I_2 + 8H_2O$

How much $KMnO_4$ are needed to oxidise 11.4 g of KNO_2 ?

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66. How many ml of $KMnO_4$ solution containing 158 g/L must be used to complete the conversion of 75 g of KI to I_2 in the acidic solution ?

$$2KMnO_4 + 10KI + 8H_2SO_4 \longrightarrow 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$$

Answers to Practice Problems

60. 0.7 kg
61. 916.2 g
62. 462.6 g
63. 0.25 mole
64. 2.27%
65. 8.47 g
66. 90.5 ml

Hints & Solutions on page 79

LIMITING REACTANT

In many cases, the substances in a mixture are not present in exactly the same amount as required by the balanced chemical equation. In such situations, one reactant is in excess over the other. The reactant which is present in lesser amount gets consumed after sometime and after that no further reaction takes place even though the other reactant is present. Thus,

the reactant which gets completely consumed in a reaction is called **limiting reactant.**

The concentration of the limiting reactant limits the amount of products formed. The other reactants present in quantities greater than those needed to react with the quantity of the limiting reagent present would be left unreacted. It is also called **excess reagent.** For example, in the reaction

$$2H_2 + O_2 \longrightarrow 2H_2O$$

if the reaction mixture contains 2 mol of H_2 and 2 mol of O_2, then only 1 mol of O_2 will be used up and 1 mol of O_2 will be left over. Therefore, in this case, *hydrogen is the limiting reactant. Oxygen is excess reactant.*

SOLVED EXAMPLES

Example 88.

In a reaction

$$A + B_2 \longrightarrow AB_2$$

identify the limiting reagent if any in the following reaction mixtures :

(i) 300 atoms of A + 200 molecules of B
(ii) 2 mol of A + 3 mol of B
(iii) 100 atoms of A + 100 molecules of B
(iv) 5 mol of A + 2.5 mol of B
(v) 2.5 mol of A + 5 mol of B. **N.C.E.R.T.**

Solution: According to the equation,
1 mole of A reacts with 1 mole of B_2 and 1 atom of A reacts with 1 molecule of B_2

(*i*) B is limiting reagent because 200 molecules of B_2 will react with 200 atoms of A and 100 atoms of A will be left in excess.
(*ii*) A is limiting reagent because 2 mole of A will react with 2 mol of B and 1 mol of B will be left in excess.
(*iii*) Both will react completely because it is stoichiometric mixture. No limiting reagent.
(*iv*) 2.5 mol of B will react with 2.5 mol of A and hence B is limiting reagent.
(*v*) 2.5 mol of A will react with 2.5 mol of B. Hence A is limiting reagent.

Example 89.

50.0 kg of N_2 (g) and 10.0 kg of H_2(g) are mixed to produce NH_3(g)
(a) Calculate the NH_3 (g) formed.
(b) Identify the limiting reagent in this reaction if any. **N.C.E.R.T.**

Solution:

$$\text{Moles of } N_2 = \frac{\text{Mass in } g}{\text{Molar mass}}$$

$$= \frac{50.0 \times 10^3}{28} = 1.786 \times 10^3 \text{ mol}$$

$$\text{Mole of } H_2 = \frac{\text{Mass in } g}{\text{Molar mass}}$$

$$= \frac{10 \times 10^3}{2} = 5.0 \times 10^3 \text{ mol}$$

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
1 mol 3 mol

According to the equation 1 mol of N_2 (*g*) requires 3 mol of H_2(*g*) for the reaction.
1.786×10^3 mol of N_2(*g*) will require H_2(*g*)
$= 3 \times 1.786 \times 10^3$
$= 5.36 \times 10^3$ mol
But moles of H_2 present = 5.0×10^3 mol
Therefore, N_2 is in excess and **dihydrogen is limiting reagent**
Now, 3 mol of H_2 (*g*) gives NH_3 (*g*) = 2 mol
5.0×10^3 mol of H_2(*g*) will give NH_3 (*g*)

$$= \frac{2}{3} \times 5.0 \times 10^3$$

$= 3.3 \times 10^3$ mol
Mass of NH_3 (*g*) formed = Moles × Molar mass
$= 3.3 \times 10^3 \times 17$
= 56.1 kg

Example 90.

3.0 g of H_2 react with 29.0 g of O_2 to yield H_2O.
(i) Which is the limiting reactant ?
(ii) Calculate the maximum amount of H_2O that can be formed.
(iii) Calculate the amount of one of the reactants which remains unreacted.

Solution: The balanced chemical equation is

$$2H_2 + O_2 \longrightarrow 2H_2O$$
2 mol 1 mol 2 mol

$$\text{Moles of } H_2 = \frac{\text{Wt. of } H_2}{\text{Molecular mass of } H_2} = \frac{3.0}{2} = 1.50 \text{ mol}$$

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$$\text{Moles of } O_2 = \frac{\text{Wt. of } O_2}{\text{Molecular mass of } O_2} = \frac{29.0}{32.0} = 0.906 \text{ mol}$$

(*i*) **Calculation of limiting reactant**

According to the above equation, 2 mol of H_2 require O_2 = 1 mol

$\therefore$ 1.50 mol of H_2 require $O_2 = \frac{1.50}{2} = 0.75$ mol

But moles of O_2 actually present = 0.906 mol

Therefore, O_2 is in excess and H_2 is the **limiting reactant.**

(*ii*) **Calculation of maximum amount of H_2O formed.**

Now, 2 mol of H_2 form H_2O = 2 mol

$\therefore$ 1.50 mol of H_2 form H_2O = 1.50 mol

Thus, the maximum amount of H_2O formed = **1.50 mol**

(*iii*) **Calculation of the amount of one of the reactants which remains unreacted i.e., O_2**

Number of moles of O_2 added = 0.906 mol

Number of moles of O_2 used up = 0.75 mol

$\therefore$ Number of moles of O_2 unreacted = 0.906 − 0.75 = **0.156 mol.**

❑ Example 91.

If 20.0 g of $CaCO_3$ is treated with 20.0 g of HCl, how many grams of CO_2 can be produced according to the reaction :

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

N.C.E.R.T.

Solution: In this problem, CO_2 can be calculated by using either of the reactants $CaCO_3$ or HCl. So, first of all we are to calculate the limiting reactant.

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

1 mol : 2 mol

40 + 12 + 3 × 16 : 2 × (1 + 35.5)

= 100 g : = 73 g

According to above equation,

100 g of $CaCO_3$ require 73 g of HCl

20 g of $CaCO_3$ require $= \frac{73}{100} \times 20 = 14.6$ g

But amount of HCl actually present = 20.0 g

Therefore, $CaCO_3$ is limiting reactant and HCl is excess reactant.

Now let us calculate the amount of CO_2 produced when entire quantity of limiting reactant reacts.

$$CaCO_3(s) + 2HCl(g) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

1 mol : 1 mol

100 g : 44 g

20 g : ?

100 g of $CaCO_3$ produces CO_2 = 44 g

20 g of $CaCO_3$ will produce $CO_2 = \frac{44}{100} \times 20$

= **8.80 g**

❑ Example 92.

Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation :

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

(i) Calculate the mass of ammonia produced if 2.00×10^3 g of dinitrogen reacts with 1.00×10^3 g of dihydrogen.

(ii) Will any of the two reactants remain unreacted ?

(iii) If yes, which one and what would be its mass ?

Solution: The balanced chemical equation is

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$\text{Moles of } N_2 = \frac{2.00 \times 10^3}{28} = 71.43 \text{ mol}$$

$$\text{Moles of } H_2 = \frac{1.00 \times 10^3}{2} = 500 \text{ mol}$$

According to above equation, 1 mol of N_2 require 3 mol of H_2.

$\therefore$ 71.43 mol of N_2 will require H_2 = 3 × 71.43 = 214.29 mol

But moles of H_2 actually present = 500 mol

$\therefore$ H_2 is in excess and will remain unreacted and N_2 is limiting reagent.

(*i*) 1 mol of N_2 react with H_2 to form NH_3 = 2 mol

71.43 mol of N_2 will react with H_2 to form NH_3

$$= \frac{2}{1} \times 71.43$$

$$= 142.86 \text{ mol}$$

Mass of NH_3 produced = 142.86 × 17 = 2428.6 g

(*ii*) Hydrogen will remain unreacted.

(*iii*) Moles of H_2 initially taken = 500 mol

Moles of H_2 reacting = 214.29 mol

Moles of H_2 remaining unreacted = 500 − 214.29 = 285.71 mol

Mass of H_2 left unreacted = 285.71 × 2 = **571.42 g**

REACTIONS IN SOLUTIONS

There are many reactions which take place in solutions. In solution generally one component is present in lesser amount and is called *solute* while the other present in excess is called the *solvent. The amount of solute present in a given quantity of solvent or solution is expressed in terms of* **concentration**.

The concentration of the solution is usually expressed in the following ways :

1. Mass percentage or volume percentage

The **mass percentage** *of a component in a given solution* is the **mass of the component per 100 g of the solution**. For example, if W_A is the mass of component A and W_B is the mass of component B in a solution, then

$$\text{Mass percentage of A} = \frac{W_A}{W_A + W_B} \times 100$$

This can be expressed as w/w. For example, a 10% (*w/w*) solution of sodium chloride means that 10 g of sodium chloride is present in 90 g of water so that the

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total mass of the solution is 100 g or simply 10 g of sodium choride is present in 100 g of solution.

Volume percentage. In case of a liquid dissolved in another liquid, it is convenient to express the concentrations in volume percentage. The **volume percentage** is defined *as* **the volume of the component per 100 parts by volume of the solution**. For example, if V_A and V_B are the volume of two components A and B respectively in a solution, then

Volume percentage of A

$$= \frac{\text{Volume of A}}{\text{Volume of A + Volume of B}} \times 100$$

This may be expressed as *v/v*. Sometimes, we express the concentrations as weight/volume. For example, a 10% solution of sodium chloride (*w/v*) means that 10 g of sodium chloride are dissolved in 100 mL of solution.

Parts per million. When a solute is present in very minute amounts (trace quantities), the concentration is expressed in *parts per million* abbreviated as **ppm. It is the parts of a component per million parts of the solution**. It is expressed as:

$$ppm \text{ A} = \frac{\text{Mass of component A}}{\text{Total mass of solution}} \times 10^6$$

For example, suppose a litre of public supply water contains about 3×10^{-3} g of chlorine. The mass percentage of chlorine is :

$$\text{Mass percentage of chlorine } \frac{3.0 \times 10^{-3}}{1000} \times 100$$

$$= 3 \times 10^{-4} \text{ (Total volume is 100 mL)}$$

The parts per million parts of chlorine is :

$$\text{or } ppm \text{ of chlorine} = \frac{3 \times 10^{-3} \times 10^6}{1000} = 3$$

Thus, instead of expressing concentration of chlorine as 3×10^{-4} % it is better to express as 3 *ppm*.

Atmospheric pollution in cities due to harmful gases is generally expressed in ppm though in this case the values refer to volumes rather than masses. For example, the concentration of SO_2 in Delhi has been found to be as high as 10 ppm. This means that 10 cm^3 of SO_2 are present in 10^6 cm^3 (or 10^3 L) of air.

The concentration of atmospheric pollutants in cities is generally expressed in terms of mg/mL.

❑ Example 93.

If 11 g of oxalic acid are dissolved in 500 mL of solution (density = 1.1 g mL^{-1}), what is the mass % of oxalic acid in solution ?

Solution : 11 g of oxalic acid are present in 500 mL of solution.

Density of solution = 1.1 g mL^{-1}

Mass of solution = (500 mL) × (1.1. g mL^{-1})

= 550 g

Mass of oxalic acid = 11 g

$$\text{Mass \% of oxalic acid} = \frac{11}{550} \times 100 = \mathbf{2\%}.$$

2. Molarity of a solution

It is **the number of moles of the solute dissolved per litre of the solution**. It is represented as 'M'. Thus, a solution which contains one gram mole of the solute dissolved per litre* of the solution, is regarded as **one molar** solution. For example, 1M Na_2CO_3 (molar mass = 106) solution has 106 g of the solute present per litre of the solution.

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litres}}$$

It is convenient to express volume in cm^3 or mL so that

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution (in mL or cm}^3\text{)}} \times 1000$$

($\because$ 1 litre = 1000 mL)

Thus, **the units of molarity are moles per litre (mol L^{-1}) or moles per cubic decimetre (mol dm^{-3})** . The symbol M is used for mol L^{-1} or mol dm^{-3} and it represents molarity.

If n_B moles of solute are present in V mL of solution, then

$$\text{Molarity} = \frac{n_B}{V} \times 1000$$

Moles of solute can be calculated as :

$$\text{Moles of solute} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}}$$

Molarity is one of the common measures of expressing concentration which is frequently used in the laboratory. However, it has one **disadvantage.** *It changes with temperature because of expansion or contraction of the liquid with temperature.*

❑ Example 94.

2.46 g of sodium hydroxide (molar mass = 40) are dissolved in water and the solution is made to 100 cm^3 in a volumetric flask. Calculate the molarity of the solution.

Solution : Amount of NaOH = 2.46 g

Volume of solution = 100 cm^3

$$\text{Moles of NaOH} = \frac{\text{Mass of NaOH}}{\text{Molar mass}}$$

$$= \frac{2.46}{40} = 0.0615 = 0.0615$$

$$\text{Molarity} = \frac{\text{Moles of NaOH}}{\text{Volume of solution}} \times 1000$$

$$= \frac{0.0615}{100} \times 1000$$

$$= \mathbf{0.615\ M.}$$

* In SI units, volume is expressed as dm^3 and 1 litre = 1 dm^3.

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3. Molality of a solution

It is **the number of moles of the solute dissolved per 1000 g (or 1 kg) of the solvent**. It is denoted by *m*. Mathematically,

$$\text{Molality } (m) = \frac{\text{Moles of solute}}{\text{Weight of solvent in kg}}$$

$$\text{or} \quad = \frac{\text{Moles of solute}}{\text{Mass of solvent in gram}} \times 1000$$

Thus, **the units of molality are moles per kilogram *i.e.*, mol kg^{-1}.** It is represented by the symbol **m**.

If n_B moles of solute are dissolved in W grams of solvent, then

$$\text{Molality} = \frac{n_B}{W} \times 1000$$

KEY POINT

From the discussion of molarity and molality, it is evident that in molarity we consider the *volume of the solution* while in molality, we take the *mass of the solvent*. Therefore, the two are never equal. **Molality is considered better for expressing the concentration as compared to molarity because the molarity changes with temperature because of expansion or contraction of the liquid with temperature. However, molality does not change with temperature because mass of the solvent does not change with change in temperature.**

❑ **Example 95.**

Calculate the molality of a solution containing 20.7 g of potassium carbonate dissolved in 500 mL of solution (assume density of solution = 1 g mL^{-1}).

Solution : Mass of K_2CO_3 = 20.7 g

Molar mass of K_2CO_3 = 138

$$\text{Moles of } K_2CO_3 = \frac{20.7}{138} = 0.15$$

Mass of solution = (500 mL) × (1 g mL^{-1}) = 500 g

Amount of water = 500 – 20.7 = 479.3 g

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent in gram}} \times 1000$$

$$= \frac{0.15}{479.3} \times 1000 = \mathbf{0.313\ m.}$$

4. Mole fraction

It is the ratio of number of moles of one component to the total number of moles (solute and solvent) present in the solution. It is denoted by *x*. Let us suppose that a solution contains n_A moles of solute and n_B moles of the solvent. Then,

$$\text{Mole fraction of solute } (x_A) = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of solvent } (x_B) = \frac{n_B}{n_A + n_B}$$

The sum of mole fractions of all the components in solution is always equal to one as shown below :

$$x_A + x_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

Thus, if the mole fraction of one component of a binary solution is known, that of the other can be calculated. For example, the mole fraction x_A is related to x_B as :

$x_A = 1 - x_B$ or $x_B = 1 - x_A$

It may be noted that the **mole fraction is independent of temperature.**

❑ **Example 96.**

A solution is prepared by adding 60 g of methyl alcohol to 120 g of water. Calculate the mole fraction of methanol and water.

Solution : Mass of methanol = 60 g

$$\text{Moles of methanol} = \frac{60}{32} = 1.875$$

(*Molar mass = 32*)

Mass of water = 120 g

$$\text{Moles of water} = \frac{120}{18} = 6.667$$

(*Molar mass = 18*)

Total number of moles = 1.875 + 6.667 = 8.542

$$\text{Mole fraction of methanol} = \frac{1.875}{8.542} = \mathbf{0.220}$$

$$\text{Mole fraction of water} = \frac{6.667}{8.542} = \mathbf{0.780.}$$

5. Normality

It is the number of gram equivalents of the solute dissolved per litre of the solution. It is denoted by N.

$$\text{Normality (N)} = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution in litres}}$$

or Normality

$$= \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution in mL}} \times 1000$$

Thus, **the units of normality are gm equivalent per litre *i.e.* g equiv L^{-1}.**

Gram equivalents of solute can be calculated as :

$$\text{Gram equivalents of solute} = \frac{\text{Mass of solute}}{\text{Equivalent mass}}$$

Like molarity, **normality of a solution also changes with temperature.**

❑ **Example 97.**

Calculate the normality of solution containing 31.5 g of hydrated oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) in 1250 mL of solution.

Solution : Mass of oxalic acid = 31.5 g

$$\text{Equivalents of oxalic acid} = \frac{31.5}{63} = 0.5$$

(Eq. wt. 126/2 = 63)

Volume of solution = 1250 mL

$$\text{Normality} = \frac{0.5}{1250} \times 1000 = \mathbf{0.4\ N.}$$

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▶ Relationship between Normality and Molarity of Solutions

The normality and molarity of a solution are related as :

$$\text{Normality} = \text{Molarity} \times \frac{\text{Molar mass}}{\text{Equivalent mass}}$$

For acids,

Normality = Molarity × Basicity

where basicity is the number of H^+ ions that a molecule of an acid can give in solution.

For bases,

Normality = Molarity × Acidity

where acidity is the number of OH^- ions that a molecule of a base can give in solution.

For example,

1 M H_2SO_4 solution = 2N H_2SO_4 solution (basicity = 2)

1 M H_3PO_4 solution = 3N H_3PO_4 solution (basicity = 3)

and 1 M $Ca(OH)_2$ solution = 2N $Ca(OH)_2$ solution (acidity = 2)

Alternatively, 1 N H_2SO_4 solution = 0.5 M H_2SO_4 solution (basicity = 2) and so on.

▶ It may be noted that these days the terms normality or equivalent weight are not commonly used.

Sometimes, the term **formality** is also used. It gives the number of formula masses of the solute dissolved per litre of the solution. It is represented by F.

$$\text{Formality} = \frac{\text{Number of formula mass of the solute}}{\text{Volume of the solution in mL}} \times 1000$$

This term is used to express the concentration of ionic substances (*e.g.* NaCl, KNO_3, $CuSO_4$) which do not exist as discrete molecules. In such cases, we do not use the term mole for expressing the concentration. The sum of the atomic masses of various atoms constituting the formula of the ionic compound is called **gram formula mass** instead of molar mass.

WATCH OUT !

- Molarity of a solution changes with temperature due to accompanied changes in volume of the solution.
- Molality and mole fraction do not change with temperature.

REMEMBER

FORMULAE TO REMEMBER

$$\textbf{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Vol. of solution (in mL)}} \times 1000$$

$$\textbf{Molality } (m) = \frac{\text{Moles of solute}}{\text{Mass of solvent (in g)}} \times 1000$$

$$\textbf{Normality (N)} = \frac{\text{Gram equiv. of solute}}{\text{Vol. of solution (in mL)}} \times 1000$$

$$\textbf{Normality} = \text{Molarity} \times \frac{\text{Mol. mass}}{\text{Eq. mass}}$$

$$\textbf{Mole fraction of solute } (x_B) = \frac{\text{Moles of solute}}{\text{Moles of solute} + \text{Moles of solvent}}$$

Mole fraction of solute + Mole fraction of solvent = 1

or Mole fraction of solvent = 1 − Mole fraction of solute

SOLVED EXAMPLES

Example 98.

A solution is prepared by dissolving 18.25 g of NaOH in distilled water to give 200 ml of solution. Calculate the molarity of the solution.

Solution: Moles of NaOH $= \frac{18.25}{40}$

(Molecular mass of NaOH = 40)

Vol. of solution = 200 mL

$$\text{Molarity} = \frac{18.25 \times 1000}{40 \times 200} = \textbf{2.28 M}$$

Example 99.

How many grams of Na_2CO_3 should be dissolved to make 100 cm^3 of 0.15 M Na_2CO_3 solution ?

Solution: 1000 cm^3 of 0.15 M Na_2CO_3 contain Na_2CO_3 = 0.15 mole

100 cm^3 of 0.15 M Na_2CO_3 contain Na_2CO_3

$$= \frac{0.15}{1000} \times 100 = 0.015 \text{ mole}$$

(Molar mass of Na_2CO_3 = 106)

Mass of Na_2CO_3 = 0.015 × 106 = **1.59 g**

Example 100.

A solution is prepared by dissolving 2 g of substance A in 18 g of water. Calculate the mass percentage of solute. ***N.C.E.R.T.***

Solution:

Mass of solute, A = 2 g

Mass of water = 18 g

Mass of solution = 2 + 18 = 20 g

$$\text{Mass percent of A} = \frac{\text{Mass of A}}{\text{Mass of solution}} \times 100 \text{ g}$$

$$= \frac{2}{20} \times 100 = \textbf{10\%}$$

Example 101.

Calculate the concentration of nitric acid in moles per litre in a sample which has a density, 1.41 g mL^{-1} and the mass percent of nitric acid in it being 69%. ***N.C.E.R.T.***

Solution:

69 mass percent of nitric acid means that 69 g of HNO_3 are present in 100 g of solution.

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$$\text{Volume of solution} = \frac{\text{Mass}}{\text{density}} = \frac{100\text{ g}}{1.41\text{ g mL}^{-1}} = 70.92\text{ mL}$$

$$\text{Moles of } HNO_3 = \frac{69}{63}$$

$$\therefore \quad \text{Molarity} = \frac{\text{Moles of } HNO_3}{\text{Volume of solution (in mL)}} \times 1000$$

$$= \frac{69/63}{70.92} \times 1000 = \mathbf{15.44\ M}$$

❑ Example 102.

A sample of $NaNO_3$ weighing 0.38 g is placed in a 250 ml volumetric flask. The flask is then filled with water to the mark on the neck. What is the molarity of the solution ?

Solution: Mass of $NaNO_3$ dissolved = 0.38 g

$$\text{Molecular mass of } NaNO_3 = 23 + 14 + 48 = 85$$

$$\text{Moles of } NaNO_3 \text{ dissolved} = \frac{0.38}{85}$$

$$\text{Volume of solution} = 250\text{ mL}$$

$$\text{Molarity} = \frac{0.38/85}{250} \times 1000 = \mathbf{0.018\ M}$$

❑ Example 103.

What is the concentration of sugar ($C_{12}H_{22}O_{11}$) in mol L^{-1} if its 20 g are dissolved in enough water to make a volume upto 2 L ? ***N.C.E.R.T.***

Solution: Mass of sugar = 20 g

$$\text{Molecular mass of sugar} = 12 \times 12 + 1 \times 22 + 11 \times 16 = 342$$

$$\text{Moles of sugar} = \frac{20}{342}$$

$$\text{Volume of solution} = 2\text{ L}$$

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Vol. of solution in L}} = \frac{20/342}{2} = \mathbf{0.029\ mol\ L^{-1}}$$

❑ Example 104.

If the density of methanol is 0.793 kgL^{-1}, what is the volume needed for making 2.5 L of its 0.25 M solution ? ***N.C.E.R.T.***

Solution: Let us calculate moles of methanol present in 2.5 L of 0.25 M solution.

$$\text{Molarity} = \frac{\text{Moles of } CH_3OH}{\text{Volume in L}}$$

$$0.25 = \frac{\text{Moles of } CH_3OH}{2.5}$$

$$\therefore \quad \text{Moles of } CH_3OH = 0.25 \times 2.5 = 0.625 \text{ moles}$$

$$\text{Mass of } CH_3OH = 0.625 \times 32 = 20\text{ g}$$

(Molecular mass of CH_3OH = 32)

Now 0.793×10^3 g of CH_3OH is present in 1000 mL

$$\text{20 g of } CH_3OH \text{ will be present in} = \frac{1000}{0.793 \times 10^3} \times 20 = \mathbf{25.2\ mL}$$

❑ Example 105.

How many moles and how many grams of sodium chloride are present in 250 mL of a 0.50 M NaCl solution ?

Solution: This can be calculated by using the formula :

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Vol. of solution (in mL)}} \times 1000$$

$$0.50 = \frac{\text{Moles of NaCl}}{250} \times 1000$$

$$\therefore \text{Moles of NaCl} = \frac{0.50 \times 250}{1000} = \mathbf{0.125\ mol}$$

Gram molecular mass of NaCl = 23 + 35.5 = 58.5 g

∴ Mass of NaCl solution in grams

= Moles of NaCl × Molecular mass

= 0.125 × 58.5 = **7.3125 g**

❑ Example 106.

Calculate the number of Cl^- ions in 100 ml of 0.001 M HCl solution.

Solution : Since HCl is a strong acid, it ionises completely so that the concentration of HCl is equal to that of Cl^- ions.

1000 ml of 0.001 M HCl solution contains Cl^- = 0.001 mole

100 ml of 0.001 M HCl solution contains Cl^-

$$= \frac{0.001 \times 100}{1000} = 1 \times 10^{-4}\text{ mole}$$

$$\text{No. of } Cl^- \text{ ions} = 6.022 \times 10^{23} \times 1.0 \times 10^{-4} = \mathbf{6.022 \times 10^{19}.}$$

❑ Example 107.

A solution of oxalic acid, $(COOH)_2.2H_2O$ is prepared by dissolving 0.63 g of the acid in 250 mL of the solution. Calculate (i) molarity and (ii) normality of the solution.

Solution : (*i*) Calculation of molarity

Molar mass of oxalic acid, $(COOH)_2 . 2H_2O$

$$= 2(12 + 32 + 1) + 2 \times 18 = 126\text{ g mol}^{-1}$$

$$\text{Moles of oxalic acid} = \frac{0.63}{126} = 0.005\text{ mol}$$

$$\text{Volume of solution} = 250\text{ mL}$$

$$\text{Molarity} = \frac{0.005 \times 1000}{250} = \mathbf{0.02\ M}$$

(*ii*) Calculation of normality

$$\text{Equivalent mass of oxalic acid} = \frac{\text{Mol. mass of oxalic acid}}{\text{Basicity}} = \frac{126}{2} = 63$$

$$\text{Gram equivalents of oxalic acid} = \frac{0.63}{63} = 0.01$$

$$\text{Normality} = \frac{\text{Gram equivalents of solute}}{\text{Volume of solution (in mL)}} \times 1000 = \frac{0.01}{250} \times 1000 = \mathbf{0.04\ N}$$

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❑ Example 108.

2.82 g of glucose (molar mass = 180) are dissolved in 30 g of water. Calculate (a) the molality (b) mole fraction of glucose and water.

Solution : (*a*) **Calculation of molality of solution.**

$$\text{Mass of glucose} = 2.82 \text{ g}$$

$$\text{Moles of glucose} = \frac{2.82}{180} \text{ (Molar mass = 180)}$$

$$\text{Mass of water} = 30 \text{ g}$$

$$\text{Molality} = \frac{\text{Moles of glucose}}{\text{Mass of water}} \times 1000$$

$$= \frac{2.82 \times 1000}{180 \times 30} = \mathbf{0.522\ m.}$$

(*b*) **Calculation of mole fraction**

$$\text{Moles of glucose} = \frac{2.82}{180} = 0.0157$$

$$\text{Moles of water} = \frac{30}{18} = 1.67$$

$$\text{Mole fraction of glucose} = \frac{0.0157}{0.0157 + 1.67} = \mathbf{0.009.}$$

$$\text{Mole fraction of water} = \frac{1.67}{0.0157 + 1.67} = \mathbf{0.991.}$$

❑ Example 109.

Calculate the molarity of pure water (density of water = 1 g mL^{-1})

Solution : Density of water = 1 g mL^{-1}

Mass of 1000 mL of water = Volume × Density

= 1000 × 1 = 1000 g

$$\text{Moles of water} = \frac{1000}{18} = 55.55$$

Now, 55.55 moles of H_2O are present in 1000 ml or 1 L of water

∴ Molarity = **55.55 M.**

❑ Example 110.

A solution is 25% water, 25% ethanol and 50% acetic acid by mass. Calculate the mole fraction of each component.

Solution : Let the total mass of solution = 100 g

Mass of water = 25 g

Mass of ethanol = 25 g

Mass of acetic acid = 50 g

$$\text{Moles of water} = \frac{25}{18} = 1.388$$

(∵ Molar mass of H_2O = 18)

$$\text{Moles of ethanol} = \frac{25}{46} = 0.543$$

(∵ Molar mass of C_2H_5OH = 46)

$$\text{Moles of acetic acid} = \frac{50}{60} = 0.833$$

(∵ Molar mass of CH_3COOH = 60)

Total number of moles = 1.388 + 0.543 + 0.833

= 2.764

$$\text{Mole fraction of water} = \frac{1.388}{2.764} = \mathbf{0.502.}$$

$$\text{Mole fraction of ethanol} = \frac{0.543}{2.764} = \mathbf{0.196.}$$

$$\text{Mole fraction of acetic acid} = \frac{0.833}{2.764} = \mathbf{0.302.}$$

❑ Example 111.

A solution of glucose in water is labelled as 10% (w/w). The density of the solution is 1.20 g mL^{-1}. Calculate

(i) molality

(ii) molarity, and

(iii) mole fraction of each component in solution.

Solution : 10% (w/w) solution of glucose means that 10 g of glucose is present in 100 g of solution or in 90 g of water.

(*i*) **Calculation of molality**

$$\text{Mass of glucose} = 10 \text{ g}$$

$$\text{Moles of glucose} = \frac{10}{180} = 0.0556$$

(Molar mass of glucose = 180)

$$\text{Mass of water} = 90 \text{ g}$$

$$\therefore \quad \text{Molality} = \frac{\text{Moles of glucose}}{\text{Mass of water}} \times 1000$$

$$= \frac{0.0556}{90} \times 1000 = \mathbf{0.618\ m.}$$

(*ii*) **Calculation of molarity**

$$\text{Moles of glucose} = 0.0556$$

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}}$$

$$= \frac{100}{1.20} = 83.3 \text{ mL}$$

$$\text{Molarity} = \frac{\text{Moles of glucose}}{\text{Vol. of solution}} \times 1000$$

$$= \frac{0.0556}{83.3} \times 1000 = \mathbf{0.667\ M.}$$

(*iii*) **Calculation of mole fraction of components**

$$\text{Moles of glucose} = 0.0556$$

$$\text{Moles of water} = \frac{90}{18} = 5.0$$

$$\text{Total moles} = 5.0 + 0.0556 = 5.0556$$

$$\text{Mole fraction of glucose} = \frac{0.0556}{5.0556} = \mathbf{0.011.}$$

$$\text{Mole fraction of water} = \frac{5.0}{5.0556} = \mathbf{0.989.}$$

❑ Example 112.

A sugar syrup of weight 214.2 g contains 34.2 g of sugar ($C_{12}H_{22}O_{11}$). Calculate :

(i) molal concentration, and

(ii) mole fraction of sugar in the syrup.

Solution : (*i*) Weight of sugar syrup = 214.2 g

Weight of sugar in syrup = 34.2 g

Weight of water in syrup = 214.2 – 34.2 = 180.0 g

$$\text{Moles of sugar} = \frac{34.2}{342} = 0.1$$

(Molar mass = 342)

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$$\text{Molality} = \frac{0.1}{180} \times 1000 = \mathbf{0.56\ m.}$$

(ii) $$\text{Moles of sugar} = \frac{34.2}{342} = 0.1$$

$$\text{Moles of water} = \frac{180}{18} = 10$$

$$\text{Mole fraction of sugar} = \frac{0.1}{10 + 0.1} = \mathbf{0.0099.}$$

Molarity Equation

To calculate the volume of a definite molarity of a solution required to prepare solution of other molarity, we can use the relation

$$M_1V_1 = M_2V_2$$

where M_1 = Initial molarity,
M_2 = Molarity of new solution
V_1 = Initial volume,
V_2 = Volume of new solution

This is known as ***molarity equation*** and is commonly used to calculate the molarity of solution after dilution.

Normality Equation

Like molarity equation, to calculate the volume of a definite normality of a solution required to prepare solution of other normality, we can use the relation :

$$N_1V_1 = N_2V_2$$

where N_1 is the initial normality of a solution having volume V_1 and N_2 is the normality of new solution having volume V_2. This is known as ***normality equation.***

Molarity equation and normality equation are **commonly used** to

(i) calculate the molarity or normality of a solution after mixing two or more solutions.

(ii) calculate the volume of the solution of given molarity or normality required to dilute to get solution of known molarity or normality. For example:

(a) If V_1 mL of a solution of molarity M_1 are mixed with V_2 mL of solution of molarity M_2, then molarity of the solution after mixing M_3 can be calculated as :

$$M_1V_1 + M_2V_2 = M_3(V_1 + V_2)$$

(b) If V_2 mL of a solution of molarity M_2 is to be prepared from a solution of molarity M_1 (concentrated) then volume of solution (say V_1) of molarity M_1 required can be calculated from the molarity equation:

$$M_1 \times V_1 = M_2 \times V_2$$

or $$V_1 = \frac{M_2 \times V_2}{M_1}$$

For example, if we want to prepare 500 mL of 0.5 M HCl solution from 10 M HCl solution, then volume of 10 M solution required can be calculated as:

$$10\ \text{M} \times V_1 = 0.5\ \text{M} \times 500\ \text{mL}$$

$$V_1 = \frac{0.5 \times 500}{10} = 25\ \text{mL}$$

$\therefore$ Volume of 10 M HCl required = 25 mL

Water to be added = 500 – 25 = 475 mL

Example 113.

Calculate the volume of 0.015 M HCl solution required to prepare 250 mL of a 5.25×10^{-3} M HCl solution.

Solution: Applying molarity equation.

$$\underbrace{M_1V_1}_{\text{Initial}} = \underbrace{M_2V_2}_{\text{Final}}$$

$$0.015\ \text{M} \times V_1 = 5.25 \times 10^{-3}\ \text{M} \times 250\ \text{mL}$$

$$\therefore \quad V_1 = \frac{5.25 \times 10^{-3} \times 250}{0.015}$$

$$= \mathbf{87.5\ mL}$$

Example 114.

250 mL of 1.5 M solution of sulphuric acid is diluted by adding 5L of water. What is the molarity of the diluted solution ?

Solution: Volume of diluted solution = 5000 + 250 = 5250 mL

Applying molarity equation

$$\underbrace{M_1V_1}_{\text{Initial}} = \underbrace{M_2V_2}_{\text{Final}}$$

$$1.5\ \text{M} \times 250\ \text{mL} = M_2 \times 5250\ \text{mL}$$

$$\therefore \quad M_2 = \frac{1.5 \times 250\ \text{mL}}{5250\ \text{mL}}$$

$$= \mathbf{0.0714\ M}$$

Example 115.

What volume of 10 M HCl and 3 M HCl should be mixed to get 1L of 6 M HCl solution?

Solution : Suppose volume of 10 M HCl required to prepare 1 L of 6 M HCl = x litre

Volume of 3 M HCl required = $(1 - x)$ litre

Applying molarity equation :

$$\underbrace{M_1V_1}_{10\ \text{M HCl}} + \underbrace{M_2V_2}_{3\ \text{M HCl}} = \underbrace{M_3V_3}_{6\ \text{M HCl}}$$

$$10 \times x + 3\,(1 - x) = 6 \times 1$$

$$10x + 3 - 3x = 6$$

$$7x = 3 \text{ or } x = \frac{3}{7} = 0.428\ \text{L}$$

$\therefore$ Vol. of 10 M HCl required = 0.428 L = **428 mL**

Vol. of 3 M HCl required = 1 – 0.428 = 0.572 L
= **572 mL**

Example 116.

Commercially available concentrated hydrochloric acid contains 38% HCl by mass.

(i) What is the molarity of the solution (density of solution = 1.19 g mL^{-1}) ?

(ii) What volume of concentrated HCl is required to make 1.0 L of an 0.10 M HCl ?

Solution: *(i)* 38% HCl by mass means that 38 g of HCl is present in 100 g of solution.

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$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{100}{1.19} = 84.03 \text{ mL}$$

$$\text{Moles of HCl} = \frac{38}{36.5} = 1.04$$

$$\text{Molarity} = \frac{1.04 \times 1000}{84.03} = \mathbf{12.38\ M}$$

(*ii*) The volume of this solution required to make 1.0 L of 0.10 M HCl can be calculated by applying molarity equation as

$$\frac{M_1V_1}{\text{acid}_1} = \frac{M_2V_2}{\text{acid}_2}$$

$$12.38 \text{ M} \times V_1 = 0.10 \text{ M} \times 1.0 \text{ L}$$

$$\therefore \quad V_1 = \frac{0.10 \times 1.0}{12.38} = 0.00808 \text{ L or } = \mathbf{8.08\ cm^3}$$

❑ Example 117.

Commercially available sulphuric acid contains 93% acid by mass and has a density of 1.84 g mL^{-1}. Calculate (i) the molarity of the solution (ii) volume of concentrated acid required to prepare 2.5 L of 0.50 M H_2SO_4

Solution: (*i*) 93% H_2SO_4 by mass means that 93 g of H_2SO_4 is present in 100 g of solution.

$$\text{Vol. of 100 g of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{100}{1.84} = 54.3 \text{ mL}$$

$$\text{Moles of } H_2SO_4 = \frac{93}{98} = 0.95 \text{ mol}$$

$$\text{Molarity} = \frac{0.95 \times 1000}{54.3} = 17.5 \text{ M}$$

(*ii*) Applying molarity equation,

$$\frac{M_1V_1}{\text{acid}_1} = \frac{M_2V_2}{\text{acid}_2}$$

$$17.5 \text{ M} \times V_1 = 0.5 \text{ M} \times 2.5 \text{ L}$$

$$\therefore \quad V_1 = \frac{0.5 \times 2.5}{17.5} = 0.071 \text{ L} = \mathbf{71\ mL}$$

Converting one concentration unit into another concentration unit.

● Calculating molality from molarity

Molality is the moles of solute dissolved per 1000g of the solvent whereas molarity is the moles of solute per 1000 mL of the solution.

Molality can be calculated from molarity of the solution as :

❒ Calculate the total mass of 1L (1000 mL) of solution by using density of the solution.

❒ Calculate mass of solute from the molarity (no. of moles) in 1L of the solution.

❒ Calculate the mass of the solvent by subtracting mass of solute from the total mass of solution.

❒ From the values of moles of solute and mass of solvent calculate molality.

❑ Example 118.

The density of 3 M solution of NaCl is 1.25 g mL^{-1}. Calculate the molality of the solution. **N.C.E.R.T.**

Solution : 3 M solution means that 3 moles of NaCl are present in 1 L solution.

Mass of NaCl in 1 L solution = 3 × 58.5
= 175.5 g
(∵ Molecular mass of NaCl = 58.5)

Density of solution = 1.25 g mL^{-1}

Mass of 1 L solution= 1000 × 1.25 = 1250 g

Mass of water in solution = 1250 – 175.5
= 1074.5 g

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in g)}} \times 1000$$

$$= \frac{3}{1074.5} \times 1000$$

$$= \mathbf{2.79\ m}$$

● Calculating molality from mole fraction

Molality is the moles of solute dissolved per 1000g of solvent whereas mole fraction is the ratio of moles of solute present to the total moles of solute and solvent present in the solution. Mole fraction also tells us that out of total of 1 mol of solution, x_{solute} mol of solute and $(1 - x)$ mol of solvent are present.

Molality can be calculated from the mole fraction as

❒ Calculate the number of moles of solvent in 1 mol of solution.

❒ Convert moles of solvent into mass of solvent.

❒ From the values of moles of solvent and mass of solvent calculate molality.

❑ Example 119.

What is the molality of a solution of methanol in water in which the mole fraction of methanol is 0.25?

Solution: 1 mole of solution contains 0.25 mol of methanol and 1 – 0.25 = 0.75 mol of water.

Mass of water = 0.75 × 18 = 13.5 g

Molality of methanol solution

$$= \frac{\text{Moles of methanol}}{\text{Mass of solvent}} \times 1000$$

$$= \frac{0.25}{13.5} \times 1000$$

$$= \mathbf{18.5\ m}$$

● Calculating mole fraction from molality

Mole fraction is the ratio of moles of solute to the total number of moles of solute and solvent whereas molality is the moles of solute dissolved in 1000 g of solvent.

Mole fraction can be calculated from the molality as

❒ Moles of solute is equal to molality of solution.

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❒ If we consider 1000 g of solvent, then calculate moles of solvent from 1000 g of solvent.

❒ From the values of moles of solute and moles of solvent, calculate mole fraction.

❑ Example 120.

What is the mole fraction of the solute in 2.5 m aqueous solution?

Solution: 2.5 m aqueous solution means that 2.5 moles of solute are present in 1000 g of water. Thus,

$$\text{Moles of solute} = 2.5 \text{ mol}$$

$$\text{Moles of water} = \frac{1000}{18} = 55.6$$

$$\text{Mole fraction of solute} = \frac{2.5}{2.5 + 55.6}$$

$$= \mathbf{0.043}$$

Practice Problems

- **67.** A sample of NaOH weighing 0.38 g is dissolved in water and the solution is made to 50.0 mL in a volumetric flask. What is the molarity of the resulting solution ? ***N.C.E.R.T.***
- **68.** The density of 3 molal solution of NaOH is 1.110 g mL^{-1}. Calculate molarity of the solution. *(NCERT Exemplar Problem)*
- **69.** A bottle contains 500 ml of 2.4 M HCl solution. How much water should be added to dilute it to 1.6 M HCl solution ?
- **70.** A bottle of concentrated sulphuric acid (density 1.80 g cm^{-3}) is labelled as 86% by weight. What is the molarity of the solution ?
- **71.** 0.63 g of oxalic acid, $(COOH)_2 .2H_2O$ are dissolved in 500 ml of solution. Calculate the molarity of the solution.
- **72.** How many moles of NaOH are contained in 27 mL of 0.15 M NaOH ?
- **73.** Calculate the number of oxalic acid molecules in 100 ml of 0.01 M oxalic acid solution.

Answers to Practice Problems

- **67.** 0.19 M
- **68.** 2.97 M
- **69.** 250 ml
- **70.** 15.8 M
- **71.** 0.01 M
- **72.** 0.00405 mol
- **73.** 6.023×10^{20}

Hints & Solutions on page 79

STOICHIOMETRY OF REACTIONS IN SOLUTIONS

Many reactions are carried out in aqueous solutions. The amounts of the product of a reaction can be calculated from the volumes of the solutions of the reactants and their concentrations. These are illustrated below:

SOLVED EXAMPLES

❑ Example 121.

250 ml of 0.5 M sodium sulphate (Na_2SO_4) solution are added to an aqueous solution containing 10.0 g of $BaCl_2$ resulting in the formation of white precipitate of $BaSO_4$. How many moles and how many grams of barium sulphate will be obtained ?

Solution: The balanced chemical equation is :

$$BaCl_2\,(aq) + Na_2SO_4\,(aq) \longrightarrow BaSO_4\,(s) + 2NaCl\,(aq)$$

Let us first calculate moles of Na_2SO_4 and $BaCl_2$

0.5 M solution of Na_2SO_4 means that 0.5 mol of Na_2SO_4 are present in 1000 mL of solution.

$$1000 \text{ mL of solution contain } Na_2SO_4 = 0.5 \text{ mol}$$

$$250 \text{ mL of solution contain } Na_2SO_4 = \frac{0.5}{1000} \times 250$$

$$= 0.125 \text{ mol}$$

$$\text{Moles of } BaCl_2 \text{ in solution} = \frac{10}{208}$$

(Mol. mass of $BaCl_2 = 137 + 2 \times 35.5 = 208$)

$$= 0.048$$

According to the balanced equation, 1 mol of $BaCl_2$ reacts with 1 mol of Na_2SO_4. Therefore, $BaCl_2$ is the limiting reactant, so only 0.048 mol of Na_2SO_4 reacts with 0.048 mol of Na_2SO_4.

Now, according to the equation,

$$1 \text{ mol of } BaCl_2 \text{ produces } BaSO_4 = 1 \text{ mol}$$

$$0.048 \text{ mol of } BaCl_2 \text{ produces } BaSO_4 = 1 \times 0.048$$

$$= \mathbf{0.048 \text{ mol}}$$

$$\text{Amount of } BaSO_4 \text{ obtained} = 0.048 \times 233$$

(Mol. mass of $BaSO_4 = 233$)

$$= \mathbf{11.18 \text{ g}}$$

❑ Example 122.

What volume of 0.6 M HCl has enough hydrochloric acid to react exactly with 25 mL of aqueous NaOH having concentration of 0.5 M ?

Solution: The balanced chemical equation is :

$$NaOH\,(aq) + HCl\,(aq) \longrightarrow NaCl\,(aq) + H_2O$$

Let us first calculate the moles of HCl and NaOH present in their solutions.

$$1000 \text{ ml of 0.5 M NaOH contains} = 0.5 \text{ mol}$$

$$25 \text{ ml of 0.5 M NaOH contain} = \frac{0.5 \times 25}{1000}$$

$$= 0.0125 \text{ mol}$$

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From the equation, it is clear that 1 mol of NaOH reacts with 1 mol of HCl. Therefore, moles of HCl required for the reaction = 0.0125 mol.

Now, we are to calculate the volume of 0.6 M HCl which contains 0.0125 mol.

0.6 mol of HCl of 0.6 M concentration are present in
= 1000 mL

0.125 mol of HCl of 0.6 M concentration are present in

$$= \frac{1000 \times 0.0125}{0.6}$$

= 20.83 mL

❑ Example 123.

What volume of 0.250 M HCl (aq) is required to react completely with 22.6 g of sodium carbonate according to the reaction :

$$Na_2CO_3\,(s) + 2HCl\,(aq) \longrightarrow 2NaCl\,(aq) + H_2O + CO_2$$

Solution: The balanced chemical equation is :

$$Na_2CO_3\,(s) + 2HCl\,(aq) \longrightarrow 2NaCl\,(aq) + H_2O + CO_2$$

1 mol 2 mol

$$\text{Moles of } Na_2CO_3 \text{ present} = \frac{22.6}{106} = 0.213$$

(Molar mass = 2 × 23 + 12 + 3 × 16 = 106)

Now, according to the equation,

1 mol of Na_2CO_3 requires moles of HCl = 2

0.213 mol of Na_2CO_3 requires moles of HCl
= 2 × 0.213 = 0.426 mol

Now, we are to calculate the volume of 0.250 M HCl containing 0.426 moles,

0.250 mole of 0.250 M HCl is present in = 1000 mL

0.426 mol of 0.250 M HCl would be present in

$$= \frac{1000}{0.250} \times 0.426 = \textbf{1704 mL.}$$

❑ Example 124.

Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction given below :

$$CaCO_3\,(s) + 2HCl\,(aq) \longrightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)$$

What mass of $CaCl_2$ will be formed when 250 mL of 0.76 M HCl react with 1000 g of $CaCO_3$? Name the limiting reagent. Calculate the number of moles of $CaCl_2$ formed in the reaction. ***(NCERT Exemplar Problem)***

Solution:

$$CaCO_3(s) + 2HCl\,(aq) \longrightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)$$

Mass of $CaCO_3$ = 1000 g

$$\text{Moles of } CaCO_3 = \frac{1000}{100} = 10 \text{ mol}$$

1000 mL of 0.76 M HCl contain HCl = 0.76 mol

$$250 \text{ mL of 0.76 M HCl contain HCl} = \frac{0.76}{1000} \times 250$$

= 0.19 mol

Now, according to the equation, 1 mol of $CaCO_3$ (*s*) requires 2 mol of HCl (*aq*). Hence, for 10 mol of $CaCO_3$(*s*), moles of HCl(*aq*) required would be

$$= \frac{2}{1} \times 10 = 20 \text{ mol}$$

But we have only 0.19 mole of HCl (*aq*)

∴ HCl (*aq*) is limiting reagent.

2 mol of HCl (*aq*) form $CaCl_2$ = 1 mol

$$0.19 \text{ mol of HCl } (aq) \text{ would form } CaCl_2 = \frac{1}{2} \times 0.19$$

= 0.095 mol

Mass of $CaCl_2$ formed = 0.095 × 111 = **10.54 g**

Practice Problems

74. What mass of solid AgCl is obtained when 25 ml of 0.068 M $AgNO_3$ reacts with excess of aqueous HCl?

75. What volume of 0.34 M KOH is sufficient to react with 20 ml of 0.15 M H_2SO_4 solution ?

76. Calculate the volume of 1.00 mol L^{-1} aqueous sodium hydroxide that is neutralised by 200 mL of 2.00 mol L^{-1} aqueous hydrochloric acid and the mass of sodium chloride produced. Neutralization reaction is

$$NaOH\,(aq) + HCl\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)$$

N.C.E.R.T.

77. In a reaction vessel 0.184 g of NaOH is required to be added for completing the reaction. How many millilitre of 0.150 M NaOH should be added for this requirement ?

78. 500 mL of 0.250 M Na_2SO_4 solution is added to an aqueous solution of 15.00 g of $BaCl_2$ resulting in the formation of the white precipitate of $BaSO_4$. How many grams of $BaSO_4$ are formed ? ***N.C.E.R.T.***

79. Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction :

$$CaCO_3\,(s) + 2HCl\,(aq) \longrightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)$$

What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 M HCl ?

Answers to Practice Problems

74. 0.24 g **75.** 17.65 mL **76.** 400 mL, 23.4 g
77. 30.7 mL
78. 16.78 g
79. 0.9375 g

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Conceptual Questions 3

CONCEPTUAL QA

Q. 1. Give two examples of molecules having molecular formula same as empirical formula.

Ans. CO_2, CH_4.

Q. 2. Give an example of molecule in which

(*i*) Ratio of molecular formula and empirical formula is 6 : 1.

(*ii*) Molecular weight is two times of the empirical formula weight.

(*iii*) The empirical formula is CH_2O and ratio of molecular formula weight and empirical formula weight is 6.

Ans. (*i*) C_6H_6 (*ii*) H_2O_2 (*iii*) $C_6H_{12}O_6$

Q.3. Write the empirical formula of *(i)* glucose *(ii)* sucrose.

Ans. (*i*) CH_2O (*ii*) $C_{12}H_{22}O_{11}$

Q. 4. What are the the SI units of molarity ?

Ans. mol dm^{-3}

Q. 5. 1.615 g of anhydrous $ZnSO_4$ was left in moist air. After a few days its weight was found to be 2.875 g. What is the molecular formula of hydrated salt ?

(At. masses : Zn = 65.5, S = 32, O = 16, H = 1)

Ans. Molecular mass of anhydrous $ZnSO_4$

$= 65.5 + 32 + 4 \times 16 = 161.5$

1.615 g of anhydrous $ZnSO_4$ combines with water

$= 2.875 - 1.1615 = 1.260$ g

1.615 g of anhydrous $ZnSO_4$ combine with water = 1.260 g

161.5 g of anhydrous $ZnSO_4$ combine with $= \frac{1.260}{1.615} \times 161.5 = 126$ g

No. of moles of water $= \frac{126}{18} = 7$

Formula : $ZnSO_4.7H_2O$.

Q. 6. Desnsity of water 1000 kg m^{-3} corresponds to ..... g cm^{-3}. Complete the statement.

Ans. 1.

Q.7 How are 0.50 m Na_2CO_3 and 0.50 M Na_2CO_3 different ?

Ans. 0.50 m Na_2CO_3 means that 0.50 moles of Na_2CO_3 are dissolved in 1000 g of water.

0.50 M Na_2CO_3 solution means that 0.50 moles of Na_2CO_3 are dissolved in 1000 mL of solution.

Q. 8. Calculate the amount of carbon dioxide that could be produced when

(*i*) 1 mol of carbon is burnt in air

(*ii*) 1 mol of carbon is burnt in 16 g dioxygen

(*iii*) 2 moles of carbon is burnt in 16 g of dioxygen.

Ans. $C + O_2 \longrightarrow CO_2$

1 mol of carbon reacts with 1 mol of oxygen to form 1 mole of CO_2.

(*i*) 1 mol of CO_2 or 44 g of CO_2.

(*ii*) Since 16 g of dioxygen *i.e.* 0.5 mol of O_2 are present, it is a limiting reagent. 0.5 mol of O_2 will form 0.5 mol of CO_2 *i.e.* 22 g.

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(*iii*) 16 g or 0.5 mol of O_2 is limiting reagent. 0.5 mol of O_2 will form 0.5 mol of CO_2 i.e. 22 g

Q. 9. In the reaction :

$$2A + 4B \longrightarrow 3C + 4D$$

when 5 moles of A react with 6 moles of B, then

(*i*) Which is the limiting reagent ?

(*ii*) Calculate the amount of C formed.

Ans. According to the equation, 2 moles of A require 4 moles of B for the reaction.

For 5 moles of A, the moles of B required

$$= \frac{4}{2} \times 5 = 10 \text{ mol}.$$

But we have only 6 moles of B.

Hence,

(*i*) B is the limiting reagent.

(*ii*) 4 moles of B give 3 mole of C.

$\therefore$ 6 moles of B will give $= \frac{3}{4} \times 6 = 4.5$ mol of C.

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Problem 8. 1.0 g of a mixture of carbonates of calcium and magnesium gave 240 mL of CO_2 at N.T.P. Calculate the percentage composition of the mixture.

Solution

$$\underset{100\text{ g}}{CaCO_3} \longrightarrow CaO + \underset{22400\text{ mL}}{CO_2}$$

$$\underset{84\text{ g}}{MgCO_3} \longrightarrow MgO + \underset{22400\text{ mL}}{CO_2}$$

Let $CaCO_3$ present in the mixture = x g

Now 100 g of $CaCO_3$ give CO_2 = 22400 mL

x g of $CaCO_3$ will give $CO_2 = \frac{22400 \times x}{100}$

$= 224\,x$ g

Similarly, 84 g of $MgCO_3$ give CO_2 = 22400 mL

$(1-x)$ g of $MgCO_3$ give $CO_2 = \frac{22400 \times (1-x)}{84}$

$= 266.7\,(1-x)$

Total CO_2 evolved at N.T.P. = 240 mL

Now, $224\,x + 266.7\,(1-x) = 240$

$224x - 266.7x = 240 - 266.7$

$-42.7x = -26.7$

$x = \frac{26.7}{42.7} = 0.625$

Wt. of $CaCO_3$ = 0.625 g

Wt. of $MgCO_3$ = 0.375 g

$\%\ CaCO_3 = \frac{0.625}{1} \times 100$

$= 62.5$

$\%\ MgCO_3 = \frac{0.375 \times 100}{1}$

$= \mathbf{37.5}$

Problem 9. 1.0 g of an alloy of aluminium and magnesium when treated with excess of dil. HCl form magnesium chloride and aluminium chloride and hydrogen collected over mercury at 0°C has a volume of 1.20 L at 0.92 atmospheric pressure. Calculate the composition of the alloy.

Solution Let us first calculate the volume of H_2 at N.T.P.

Applying $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$

$p_1 = 0.92$ atm $\quad p_2 = 1$ atm

$V_1 = 1.20$ L $\quad V_2 = ?$

$T_1 = 273$ K $\quad T_2 = 273$ K

$\therefore V_2 = \frac{p_1V_1T_2}{p_2T_1} = \frac{0.92 \times 1.20 \times 273}{1 \times 273}$

$= 1.104$ L

Let mass of Al in alloy = x g

Mass of Mg in alloy = $(1-x)$ g

$$\underset{2 \times 27 = 54\text{ g}}{2Al} + 6HCl \longrightarrow AlCl_3 + \underset{3 \times 22.4 = 67.2\text{ L}}{3H_2}$$

$$\underset{24\text{ g}}{Mg} + 2HCl \longrightarrow MgCl_2 + \underset{22.4\text{ L}}{H_2}$$

54 g of Al give H_2 at N.T.P. = 67.2 L

x g of Al give H_2 at N.T.P. $= \frac{67.2 \times x}{54}$

Similarly, 24 g of Mg give H_2 at N.T.P. = 22.4 L

$(1-x)$ g of Mg will give H_2 at N.T.P. $= \frac{22.4}{24} \times (1-x)$

Total H_2 liberated

$$\frac{67.2x}{54} + \frac{22.4(1-x)}{24} = 1.104$$

Solving for x, we get

$x = 0.5486$ g

$\therefore$ Mass of Al in the alloy = 0.5486 g

$\%$ of Al $= \frac{0.5486}{1} \times 100 = \mathbf{54.86}$

$\%$ of Mg in alloy $= 100 - 54.86 = \mathbf{45.14}$.

Problem 10. A mixture of sodium iodide and sodium chloride when treated with sulphuric acid gave sodium sulphate equal to the weight of the original mixture. Find the percentage composition of the mixture.

Solution

$$\underset{2(23+127) = 300}{2NaI} + H_2SO_4 \longrightarrow \underset{46+32+64 = 142}{Na_2SO_4} + 2HI$$

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$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$$
$$2(23 + 35.5) = 117 \qquad 46 + 32 + 64 = 142$$

Let the wt. of mixture = 1 g

Wt. of NaI in the mixture = x g

Wt. of NaCl in the mixture = $(1 - x)$ g

Now, 300 g of NaI give Na_2SO_4 = 142 g

$$x \text{ g of NaI give } Na_2SO_4 = \frac{142}{300} \times x$$

Similarly,

117 g of NaCl give Na_2SO_4 = 142 g

$$(1 - x) \text{ g of NaCl give } Na_2SO_4 = \frac{142}{117} \times (1 - x)$$

Weight of Na_2SO_4 formed = Wt. of original mixture

$$\frac{142}{300} x + \frac{142}{117} \times (1 - x) = 1$$

Solving for x, we get

$$x = 0.2886 \text{ g}$$

$$\therefore \quad \text{Wt. of NaI} = 0.2886$$

$$\% \text{ NaI in mixture} = \frac{0.2886}{1} \times 100 = \mathbf{28.86\%}$$

$$\% \text{ NaCl in mixture} = 100 - 28.86 = \mathbf{71.14\%}$$

Problem 11. How many mL of H_2SO_4 of density 1.8 g/mL containing 92.5% by volume of H_2SO_4 should be added to 1 litre of 40% solution of H_2SO_4 (density 1.30 g/mL) in order to prepare 50% solution of H_2SO_4 (density 1.4 g/mL) ?

Solution Molarity of solution containing 92.5% H_2SO_4 may be calculated as :

$$\text{Molarity } (M_1) = \frac{\text{Vol. of } H_2SO_4 \times \text{Density} \times 1000}{98 \times 100}$$

$$= \frac{92.5 \times 1.8 \times 1000}{98 \times 100} = 16.99 \text{ M}$$

Molarity of solution containing 40% H_2SO_4,

$$M_2 = \frac{40 \times 1.3 \times 1000}{98 \times 100} = 5.31 \text{ M}$$

Molarity of required solution containing 50% H_2SO_4,

$$M = \frac{50 \times 1.4 \times 1000}{98 \times 100} = 7.14 \text{ M}$$

Let V litre of solution with molarity (M_1) is added to 1 litre of solution with molarity (M_2) to prepare (1 + V) litre of solution with molarity M, then

$$M_1V_1 + M_2V_2 = MV$$
$$16.99 \times V + 5.31 \times 1 = 7.14 (1 + V)$$
$$9.85V = 1.83$$
$$V = \frac{1.83}{9.85} = 0.186 \text{ L}$$

or V = 0.186 litre or = **186 mL.**

Problem 12. You are given one litre of 0.15 M HCl and one litre of 0.40 M HCl. What is the maximum volume of 0.25 M HCl which you can make from these solutions without adding any water ?

Solution Since no water is added, the volume of 0.25 M HCl cannot be more than 2 litres. Let x litre of 0.40 M HCl (more concentrated) be added to 1 litre of 0.15 M HCl.

Applying molarity equation :

$$M_1V_1 + M_2V_2 = M_3V_3$$
$$0.15 \times 1 + 0.40 \times x = 0.25 \times (1 + x)$$

(Total volume V_3 becomes $1 + x$ litres)

$$0.15 + 0.40\,x = 0.25 + 0.25\,x$$
$$0.40x - 0.25\,x = 0.25 - 0.15$$
$$0.15\,x = 0.10$$
$$x = \frac{0.10}{0.15} = 0.667 \text{ litre}$$

Total volume of 0.25 M solution = $1 + x$

$$= 1 + 0.667 = \mathbf{1.667\ L}$$

Problem 13. A mixture of FeO and Fe_3O_4 when heated in air to a constant mass gains 5% by mass. Calculate the composition of the mixture (atomic mass of Fe = 55.8).

Solution The chemical equations are:

$$2FeO + \frac{1}{2} O_2 \longrightarrow Fe_2O_3 \qquad \ldots (i)$$
$$2(55.8 + 16) = 143.6 \qquad 2 \times 55.6 + 3 \times 16 = 159.6$$

$$2Fe_3O_4 + \frac{1}{2} O_2 \longrightarrow 3Fe_2O_3 \qquad \ldots (ii)$$
$$2(55.6 \times 3 + 4 \times 16) = 462.8 \qquad 3(2 \times 55.6 + 3 \times 16) = 478.8$$

Let the weight of mixture = 100 g

Weight of FeO = x g

Weight of Fe_3O_4 = $(100 - x)$ g

According to equation (i),

143.6 g of FeO produce Fe_2O_3 = 159.6 g

$$x \text{ g of FeO produce } Fe_2O_3 = \frac{159.6}{143.6} \times x$$

According to equation (ii)

462.8 g of Fe_3O_4 produce Fe_2O_3 = 478.8 g

$$(100 - x) \text{ g of } Fe_3O_4 \text{ produce } Fe_2O_3 = \frac{478.8}{462.8} \times (100 - x)$$

Total mass of Fe_2O_3 formed by heating

$$\frac{159.6}{143.6} x + \frac{478.8}{462.8} (100 - x)$$

$$\text{Gain in weight of mixture} = \frac{100 \times 5}{100} = 5 \text{ g}$$

Total Fe_2O_3 formed = 100 + 5 = 105 g

$$\therefore \frac{159.6}{143.6} x + \frac{478.8}{462.8} (100 - x) = 105$$

Solving, we get $x = 19.92$

$\therefore$ Mass of FeO = 19.92

Mass of Fe_3O_4 = 100 – 19.92 = 80.08

$$\text{Mass \% FeO} = \frac{19.92}{100} \times 100 = \mathbf{19.92}$$

Mass % Fe_3O_4 = **80.08.**

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Problem 14. Gastric juice contains about 3 mg of HCl per millilitre. If a person produces about 225 mL of gastric juice per day, how many antacid tablets each containing 250 mg of $Al(OH)_3$ are needed to neutralise all the HCl produced in one day ?

Solution HCl and $Al(OH)_3$ react as

$$\underset{36.5\times3 = 109.5}{3HCl} + \underset{78}{Al(OH)_3} \longrightarrow AlCl_3 + 3H_2O$$

Volume of gastric juice produced per day = 225 mL

Mass of HCl produced per day = $225 \times 3 \times 10^{-3}$
= 0.675 g

Now 109.5 g of HCl require $Al(OH)_3$ = 78 g

0.675 g of HCl will require $Al(OH)_3 = \frac{78}{109.5} \times 0.675$
= 0.481 g

Number of tablets required = $\frac{0.48}{0.250} = 1.92$
= 2 tablets.

Problem 15. A mixture of formic acid and oxalic acid is heated with concentrated H_2SO_4. The gas produced is collected and on its treatment with KOH solution, the volume of the solution decreases by 1/6th. Calculate the molar ratio of the two acids in the original mixture.

Solution Let x moles of formic acid and y moles of oxalic acid are heated.

$$\underset{x \text{ mol}}{HCOOH} \xrightarrow{\text{Conc. } H_2SO_4} \underset{x \text{ mol}}{H_2O + CO}$$

$$\underset{y \text{ mol}}{\begin{matrix}COOH\\|\\COOH\end{matrix}} \xrightarrow{\text{Conc. } H_2SO_4} \underset{y \text{ mol}}{H_2O + CO} + \underset{y \text{ mol}}{CO_2}$$

Total moles of gaseous mixture
= moles of CO + moles of CO_2
$= x + y + y = x + 2y$

KOH absorbs only CO_2 *i.e.* volume occupied by (y) moles. Under same conditions, ratios of volumes will be proportional to molar ratio of gases

$$\frac{\text{Moles of } CO_2}{\text{Moles of both gases}} = \frac{y}{x + 2y} = \frac{1}{6}$$

$6y = x + 2y$ or $4y = x$

or $\frac{x}{y} = 4$

$\therefore$ Ratio of $\begin{matrix}COOH\\|\\COOH\end{matrix}$: $\begin{matrix}COOH\\|\\COOH\end{matrix}$ **= 4 : 1.**

Problem 16. (*a*) Calculate the number of chloride ions in 100 mL of 0.01 M $AlCl_3$ solution.
(*b*) What will be the change in number of chloride ions if the solution is diluted by 100 mL water?

Solution (*a*) Molarity = $\frac{\text{Moles of } AlCl_3}{\text{Vol. of solution}} \times 1000$

$\therefore$ Moles of $AlCl_3 = \frac{\text{Molarity} \times \text{Vol. of Solution}}{1000}$

$= \frac{0.01 \times 100}{1000} = 0.001$ mol

Now, 1 molecule of $AlCl_3$ contains 3 Cl^- ions
$\therefore$ 1 mol of $AlCl_3$ contains 3 mol of Cl^- ions
0.001 mol of $AlCl_3$ contains Cl^- ions = 0.001×3
= 0.003 mol
1 mol of Cl^- ions = 6.022×10^{23} Cl^- ions
0.003 mol of Cl^- ions = $6.022 \times 10^{23} \times 0.003$
= 1.81×10^{21} Cl^- ions

(*b*) No change in number of Cl^- ions.

Solution File — Hints & Solutions for Practice Problems

3. Each side of cube = 76 mm = 7.6 cm
Volume of cubic block of ice = $(\text{side})^3$
= $(7.6 \text{ cm})^3 = 439 \text{ cm}^3$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$\therefore$ Mass = Density × Volume
= $(0.921 \text{ g cm}^{-3}) \times (439 \text{ cm}^3)$
= 404.3 or **4.0×10^2 g**
Rounded off to two significant figures as in 7.6.

5. (*a*) $\frac{108}{7.2}$ =15. (upto 2 significant numbers)

(*b*) $(1.6 \times 10^2)^2 = 2.56 \times 10^4$
or = 2.6×10^4 (upto 2 significant numbers)

(*c*) $\frac{(1.35\times10^{-6})(0.4)}{5.6} = 0.096 \times 10^{-6} = 0.1 \times 10^{-6}$
or = 1×10^{-7} (upto one significant figure)

(*d*) $\frac{3.25 \times 0.08621}{4.002} = 0.0700$ (upto 3 significant figures)

(*e*) (1.0042 – 0.0034) (1.23)
(1.0008) (1.23) = 1.23 (upto 3 significant figures)

6. (*i*) Area of square = $(\text{side})^2$
= $(1.2)^2 = 1.44 \text{ m}^2$
Correct answer = **1.4 m^2** (upto 2 significant places).

(*ii*) Volume of sphere = $\frac{4}{3}\pi r^3$

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$= \frac{4}{3} \times \frac{22}{7} \times (1.6)^3$

$= 17.164$

$=$ **17 cm^3** (upto two significant figures).

(*iii*) Length of rectangle $= \frac{\text{Area}}{\text{Breadth}} = \frac{10.25}{2.5}$

= 4.1 m (upto 2 significant figures).

Q 7. (*i*) $(1.20 \times 10^{-6}) + (6.00 \times 10^{-5})$

$0.120 \times 10^{-5} + 6.00 \times 10^{-5}$ **$= 6.12 \times 10^{-5}$.**

(upto second place of decimal as in 6.00×10^{-5})

(*ii*) $(2.164 \times 10^5)^{1/2} = (21.64 \times 10^4)^{1/2} = 4.6519 \times 10^2$

$= 4.652 \times 10^2$ (upto 4 significant figures)

(*iii*) $(9.13 \times 10^{-2})\,(7.006 \times 10^{-3}) = 63.9648 \times 10^{-5}$

$= 64.0 \times 10^{-5}$ (upto 3 significant figures)

or $= 6.40 \times 10^{-4}$

(*iv*) $4.00 \times 10^{-2} + 3.26 \times 10^{-3} + 1 \times 10^{-6}$

4.00×10^{-2}

0.326×10^{-2}

$\frac{0.0001 \times 10^{-2}}{4.3261 \times 10^{-2}}$ **$= 4.33 \times 10^{-2}$**

(upto second place of decimal).

Q 8. (*i*) $\frac{2.36 \times 0.07251}{2.130}$ = upto **three significant figures** because 2.36 contains 3 significant figures.

(*ii*) $\frac{(28.2-21.2)(1.79 \times 10^6)}{1.62}$ = upto **two significant figures** because difference of 28.2 − 21.2 *i.e.* 7.0 contains 2 significant figures.

Q 10. $(3.0 \times 10^8\ \text{ms}^{-1}) \times (2.00 \times 10^{-9}\text{s}) = 6.0 \times 10^{-1} = 0.60$ m answer should be in two significant figures as in 3.0×10^8.

Q 11. Unit factor $= \frac{0.1(\text{nm})}{1(\text{Å})}$

$\therefore$ 5896 Å $= 5896\text{Å} \times \frac{0.1(\text{nm})}{1(\text{Å})}$

= 589.6 nm.

Q 12. 1m $= 10^2$ cm

1m$^3 = (10^2\ \text{cm})^3 =$ **10^6 cm^3.**

Q 13. (*i*) 1kg = 1000 g; 1 litre = 10^3 mL

Unit factor : $1 = \frac{1000\text{g}}{\text{kg}}$; Unit factor : $1 = \frac{1\ \text{litre}}{10^3\text{mL}}$

$\therefore$ $\frac{4.86\ \text{kg}}{\text{L}} = \frac{4.86\ \text{kg}}{\text{L}} \times \frac{1000\ \text{g}}{\text{kg}} \times \frac{\text{litre}}{10^3\text{mL}}$ **= 4.86 g/mL.**

(*ii*) 1.86 km to cm

1 km $= 10^5$ cm

Unit factor : $1 = \frac{10^5\ \text{cm}}{(\text{km})}$

1.86 km = 1.86 km $\times \frac{10^5\ \text{cm}}{(\text{km})}$ **= 1.86 × 10^5 cm.**

(*iii*) 1 m = 10^6 µm

Unit factor : $1 = \frac{10^6\ \mu\text{m}}{\text{m}}$

$\therefore$ 6.92×10^{-7} m $\times \frac{10^6\ \mu\text{m}}{\text{m}}$ **= 0.692 µm**

6.92×10^{-7} m to Angstroms

1Å $= 10^{-10}$ m

Unit factor : $1 = \frac{1\text{Å}}{10^{-10}\text{m}}$

$\therefore$ 6.92×10^{-7} m $\times \frac{1\text{Å}}{10^{-10}\text{m}}$ **= 6920Å.**

(*iv*) 1 litre $= 10^3$ cm^3

Unit factor : $1 = \frac{1\ \text{litre}}{10^3\text{cm}^3}$

9.2×10^{-3} cm^3 $= 9.2 \times 10^{-3}$ cm^3 $\times \frac{1\ \text{litre}}{10^3\text{cm}^3}$

$= 9.2 \times 10^{-6}$ litre.

Q 14. Capacity of tank = length × breadth × depth

$= 0.8\ \text{m} \times 0.1\ \text{m} \times 50 \times 10^{-3}\ \text{m}$

$= 0.004$ or 4×10^{-3} m^3

1 litre $= 10^{-3}$ m^3

Unit factor : $1 = \frac{1\ \text{litre}}{10^{-3}\text{m}^3}$

$\therefore$ 4×10^{-3} m$^3 = 4 \times 10^{-3}$ m$^3 \times \frac{1\ \text{litre}}{10^{-3}\text{m}^3}$ **= 4 litre.**

Q 15. 100 L $= 100 \times 10^3$ cm^3 (1L $= 10^3$ cm^3)

$= 10^5$ cm^3.

Q 16. (*i*) 500 mg in kilogram

500 mg $= 500 \times 10^6$ g

1 kg $= 10^3$ g

Unit factor : $1 = \frac{1\text{kg}}{10^3\text{g}}$

$500 \times 10^6\ g = 500 \times 10^6 \times \frac{1\text{kg}}{10^3\text{g}} = 500 \times 10^3$ kg

$= 5.0 \times 10^5$ kg.

(*ii*) 1 kg $= 10^3$ g

Unit factor : $1 = \frac{1\,\text{kg}}{10^3\text{g}}$

$\therefore$ 3.34×10^{-24} g $= 3.34 \times 10^{-24}$ g $\times \frac{1\,\text{kg}}{10^3\text{g}}$

$= 3.34 \times 10^{-27}$ kg.

Q 17. (*i*) 1 pm $= 10^{-12}$ m, 1m $= 10^3$ mm

$\therefore$ 1pm $= 10^{-12}$ m $= 10^{-9}$ mm

Unit factor : $1 = \frac{1\ \text{pm}}{10^{-9}\text{mm}}$

1 µs $= 10^{-6}$ s

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Unit factor : 1 = $\frac{1\ \mu s}{10^{-6} s}$ or = $\frac{10^{-6} s}{1\ \mu s}$

$1.54\ mms^{-1} = 1.54\ mms^{-1} \times \frac{1\ pm}{10^{-9} mm} \times \frac{10^{-6} s}{1\ \mu s}$

$= \mathbf{1.54 \times 10^3\ pm\ \mu s^{-1}}$.

(*ii*) $1g = 1000\ mg$

Unit factor : 1 = $\frac{1000\ mg}{1g}$

$10\ dL = 1L$

Unit factor : 1 = $\frac{10\ dL}{1L} = \frac{1dL^{-1}}{10\ L^{-1}}$

$\therefore\ 25\ g\ L^{-1} = 25 gL^{-1} \times \frac{1000\ mg}{1g} \times \frac{1dL^{-1}}{10\ L^{-1}}$

$= \mathbf{2.5 \times 10^3 mg\ dL^{-1}}$.

(*iii*) $1L = 1dm^3$

Unit factor : 1 = $\frac{1dm^3}{1L}$

$10^3 dm^3 = 1m^3$

Unit factor : 1 = $\frac{1m^3}{10^3 dm^3}$

$\therefore\ 25\ L = 25\ L \times \frac{1dm^3}{1L} \times \frac{1m^3}{10^3 dm^3} = \mathbf{2.5 \times 10^{-2}\ m^3}$.

(*iv*) $1\mu g = 10^{-6} g$

Unit factor : 1 = $\frac{1\mu g}{10^{-6} g}$

$1\ m^3 = 10^6\ cm^3$

Unit factor : 1 = $\frac{10^6 cm^3}{1m^3}$

$1\ m^3 = (10^6)^3 \mu m$

Unit factor : 1 = $\frac{10^{-18} \mu m}{1m^3}$ or $\frac{1m^3}{10^{18} \mu m^3}$

$\therefore\ \frac{2.66\ g}{cm^3} \times \frac{1\ \mu g}{10^{-6} g} \times \frac{10^6 cm^3}{1m^3} \times \frac{1m^3}{10^{18} \mu m}$

$= \mathbf{2.66 \times 10^{-6}\ \mu g\ \mu m^{-3}}$.

(*v*) $1L = 1000\ mL$

Unit factor : 1 = $\frac{1000\ mL}{1L}$

$1h = 3600\ s$

Unit factor : 1 = $\frac{1h}{3600\ s}$

$\therefore\ \frac{4.2\ L}{h^2} = \frac{4.2\ L}{h^2} \times \left(\frac{1000\ mL}{1L}\right) \times \left(\frac{1h}{3600\ s}\right)^2$

$= \mathbf{3.2 \times 10^{-4}\ mL\ s^{-2}}$

18. (*i*) $1\ nm = 10^{-9}\ m$

Unit factor : 1 = $\frac{10^{-9} m}{1\ nm}$

$\therefore\ 7\ nm = 7nm \times \left(\frac{10^{-9} m}{1\ nm}\right) = \mathbf{7 \times 10^{-9}\ m}$.

(*ii*) $1\ pm = 10^{-12}\ m$

$1 = \frac{10^{-12} m}{1\ pm}$

$\therefore\ 41\ pm = 41\ pm \times \left(\frac{10^{-12} m}{1\ pm}\right) = \mathbf{41 \times 10^{-12}\ m}$.

19. Unit factor : 1 = $\frac{24\ h}{1\ day}$

$1\ hr = 60\ min$

Unit factor : 1 = $\frac{60\ min}{1\ hr}$

$1\ min = 60s$

Unit factor : 1 = $\frac{60s}{1\ min}$

$\therefore\ 2\ days = 2day \times \left(\frac{24\ h}{1\ day}\right) \times \left(\frac{60\ min}{1\ h}\right) \times \left(\frac{60\ s}{1\ min}\right)$

$= \mathbf{172800\ s}$

20. (*i*) $1\ pm = 10^{-12}\ m$

Unit factor : 1 = $\frac{10^{-12}}{1\ pm}$

$28.7\ pm = 28.7\ pm \times \left(\frac{10^{-12} m}{1\ pm}\right) = \mathbf{2.87 \times 10^{-11} m}$

(*ii*) $1\ \mu s = 10^{-6}\ s$

Unit factor : 1 = $\frac{10^{-6} s}{1\ \mu s}$

$\therefore\ 15.15\ \mu s = 15.15 \mu s \times \left(\frac{10^{-6} s}{1\ \mu s}\right) = \mathbf{1.515 \times 10^{-5}\ s}$

(*iii*) $1\ mg = 10^{-6} g$

Unit factor : 1 = $\frac{10^{-6} kg}{1\ mg}$

$\therefore\ 25365\ mg = 25365\ mg \times \left(\frac{10^{-6} kg}{1\ mg}\right)$

$= \mathbf{2.5365 \times 10^{-2}\ kg}$

21. Mass of reactants = 4.2 g + 10.0 g = 14.2 g

Mass of products = 2.2 g + 12.0 g = 14.2 g

$\therefore$ Mass of reactants = Mass of products

22. In H_2O_2,

Mass of hydrogen = 5.93 g

Mass of oxygen = 100 – 5.93 = 94.07 g

In water,

Hydrogen = 11.2 g

Oxygen = 100 – 11.2 = 88.8 g

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Let us fix the mass of hydrogen = 1.0 g
In H_2O_2,

Mass of oxygen combining with 5.93 g of hydrogen = 94.07 g
Mass of oxygen combining with 1 g of hydrogen

$$= \frac{94.07}{5.93} = \mathbf{15.86\ g}$$

In H_2O,
Mass of oxygen combining with 11.2 g of hydrogen = 88.8 g
Mass of oxygen combining with 1 g of hydrogen

$$= \frac{88.8}{11.2} = 7.93\ g$$

The ratio of masses of oxygen combining with 1g of hydrogen

15.86 : 7.93
2 : 1

This is simple ratio and therefore, it illustrates the law of multiple proportions.

23. Let us fix the mass of A to be 1.0 g
In compound X,
0.3 g of A combines with B = 0.4 g

$$1.0\ g \text{ of A will combine with B} = \frac{0.4}{0.3} \times 1.0 = \mathbf{1.33\ g}$$

In compound Y,
18 g of A combine with B = 48 g

$$1\ g \text{ of A will combine with B} = \frac{48}{18} \times 1 = \mathbf{2.66\ g}$$

The ratio of masses of B which combine with fixed weight of A (*i.e.* 1 g).

1.33 : 2.66
1 : 2

This is a simple ratio and hence it illustrates the law of multiple proportions.

24. Let us fix the mass of carbon as 1 g.
In compound A,
75 g of carbon combine with hydrogen = 25 g
1 g of carbon combines with hydrogen

$$= \frac{25}{75} = \mathbf{0.333\ g}$$

In compound B,
85.7 g of carbon combine with hydrogen = 14.3 g
1 g of carbon combines with hydrogen

$$= \frac{14.3}{85.7} = \mathbf{0.167\ g}$$

In compound C,
92.3 g of carbon combine with hydrogen = 7.7 g
1 g of carbon combines with hydrogen

$$= \frac{7.7}{92.3} = \mathbf{0.083\ g}$$

The ratio of masses of hydrogen which combine with fixed mass of carbon (i.e. 1 g)

0.333 : 0.167 : 0.083
4 : 2 : 1

This is simple whole number ratio and therefore, it illustrates the law of multiple proportions.

25. *First experiment*

Mass of copper oxide = 1.375 g
Copper left = 1.098 g
Mass of oxygen present = 1.375 – 1.098 = 0.277 g

$$\%\text{ of oxygen in CuO} = \frac{0.277 \times 100}{1.375} = \mathbf{20.14}$$

Second experiment

Mass of copper taken = 1.178 g
Mass of CuO formed = 1.476 g
Mass of oxygen present = 1.476 – 1.178 = 0.298

$$\%\text{ of oxygen in CuO} = \frac{0.298 \times 100}{1.476} = \mathbf{20.19}$$

Percentage of oxygen in the two compounds is the same, therefore, these results illustrate the law of constant composition.

26. (*i*) 22400 mL of SO_2 at N.T.P = 64 g

$$224\ mL \text{ of } SO_2 \text{ at N.T.P} = \frac{64}{22400} \times 224 = 0.64\ g$$

Mass of sulphur present = 0.32 g
Mass of oxygen present = 0.64 – 0.32 = 0.32 g

$$\%\text{ of sulphur} = \frac{0.32}{0.64} \times 100 = \mathbf{50\%}$$

(*ii*) Percentage of sulphur in second sample = **50%**
Since percentage of sulphur in two compounds is the same, therefore, these results illustrate the law of definite proportions.

27. Mass of Cu = 25.45%
Mass of H_2O = 36.07%
100 g of crystalline copper sulphate sample contain copper = 25.45
40 g of crystalline copper sulphate sample will contain copper

$$= \frac{25.45}{100} \times 40 = \mathbf{10.18\ g}$$

28. *In copper sulphide,*

Percentage of Cu = 66.5
Percentage of sulphur = 100 – 66.5 = 33.5

66.5 g of Cu combine with 33.5 g of sulphur in copper sulphide.

In copper oxide,

Percentage of Cu = 79.9
Percentage of oxygen = 100 – 79.9 = 20.1

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Solution File

79.9 g of Cu combine with 20.1 g of oxygen in copper oxide.

Let us fix the mass of copper as 1 g

In copper sulphide,

66.5 g of copper combine with sulphur = 33.5 g

1 g of copper will combine with sulphur

$$= \frac{33.5}{66.5} = \mathbf{0.503\ g}$$

In copper oxide,

79.9 g of Cu combine with oxygen =2 0.1 g

1 g of Cu will combine with oxygen

$$= \frac{20.1}{79.9} = \mathbf{0.251\ g}$$

The ratio of weights of sulphur and oxygen which combine with the fixed mass of copper (1 g)

$$0.503 \ : \ 0.251$$
$$\mathbf{2} \ : \ \mathbf{1} \qquad ...(i)$$

In sulphur trioxide,

Percentage of sulphur = 40

Percentage of oxygen = 60

The ratio of sulphur and oxygen in sulphur trioxide

$$40 \ : \ 60$$
$$2 \ : \ 3 \qquad ...(ii)$$

The ratios (*i*) and (*ii*) are

$$\frac{2}{1} \ : \ \frac{2}{3} \quad \text{or} \quad \mathbf{3:1}$$

This is a simple ratio. Hence law of reciprocal proportions is illustrated.

29. *Calculation of weights of oxygen in each oxide.*

Mass of each oxide taken = 1 g

18 g of $H_2O \equiv$16 g of oxygen

$\therefore$ 0.1254 g of water in first oxide contains oxygen

$$= \frac{16}{18} \times 0.1254 = 0.1115\ g$$

0.2263 g of water in second oxide contains oxygen

$$= \frac{16}{18} \times 0.2263 = 0.2011\ g$$

In first oxide

Mass of oxygen = 0.1115 g

Mass of metal =1 – 0.1115 = 0.8885 g

In second oxide

Mass of oxygen = 0.2011 g

Mass of metal = 1 – 0.2011 = 0.7989 g

Let us fix the weight of metal as 1 g

First oxide

Mass of oxygen which combines with 0.8885 g of metal = 0.1115 g

Mass of oxygen which combines with 1 g of metal

$$= \frac{0.1115}{0.8885} \times 1 = \mathbf{0.1255\ g}$$

Second oxide

Mass of oxygen which combines with 0.7989 g of metal = 0.2011 g

Mass of oxygen which combines with 1 g of metal

$$= \frac{0.2011}{0.7989} = \mathbf{0.2517\ g}$$

The ratio of masses of oxygen which combine with fixed mass of metal (1 gram)

$$0.1255 \ : \ 0.2517$$
$$\mathbf{1 \ : \ 2}$$

Since this is a simple ratio, therefore the above data illustrates the law of multiple proportions.

30. Average atomic mass of Si

$$= \frac{28 \times 92.25 + 29 \times 4.65 + 30 \times 3.10}{100}$$

$$= \mathbf{28.11\ u.}$$

31. (*a*) 1.6 gram atoms of oxygen = $16 \times 1.6 = \mathbf{25.6\ g.}$

(*b*) 5.6 gram atoms of sulphur = $\frac{32}{1} \times 5.6$

$= \mathbf{179.2\ g.}$

(*c*) 2.4 gram atoms of iodine = $127 \times 2.4 = \mathbf{304.8\ g.}$

32. (*i*) 2.5 gram molecules of $H_2S = 34 \times 2.5 = \mathbf{85\ g.}$

(*ii*) 3.6 gram molecules of glucose = $180 \times 3.6 = \mathbf{648\ g}$

(Molecular mass of glucose = $12 \times 6 + 1 \times 12 + 16 \times 6$

$= 180$

33. (*i*)Atomic mass of iron = 55.8

55.8 g of iron $\equiv$ 1 gram atom

669.6 g of iron = $\frac{1}{55.8} \times 669.6 = \mathbf{12\ gram\ atom.}$

(*ii*) Molecular mass of C_2H_5OH

$= 2 \times 12 + 5 \times 1 + 1 \times 16 + 1 \times 1 = 46$

46 g of C_2H_5OH = 1 gram molecule

73.6 g of $C_2H_5OH = \frac{1}{46} \times 73.6$

$= \mathbf{1.6\ gram\ molecule.}$

34. (*a*) 2.6 gram atoms of sulphur = $2.6 \times 32 = 83.2$ g

(*b*) 2.6 gram molecule of sucrose = $2.6 \times 342 = 889.2$g

(*c*) 2.60 g of iodine

$\therefore$ **Maximum mass is of 2.6 gram molecule of sucrose (*b*)**

35. (*i*) $6..022 \times 10^{23}$ atoms of calcium have mass = 40 g

1 atom of calcium has mass = $\frac{40}{6.022 \times 10^{23}}$

$= \mathbf{6.64 \times 10^{-23}\ g.}$

(*ii*) Mass of 6.022×10^{23} molecules of SO_2 = 64 g

Mass of 1 molecule of $SO_2 = \frac{64}{6.022 \times 10^{23}}$

$= \mathbf{1.06 \times 10^{-22}\ g.}$

36. (*i*) 1 mole atoms of carbon = 6.022×10^{23} atoms

0.5 mole atoms of carbon = $6.022 \times 10^{23} \times 0.5$

$= \mathbf{3.01 \times 10^{23}\ atoms.}$

(*ii*) 32 g of sulphur = 6.022×10^{23} atoms

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3.2 g of sulphur = $\frac{6.022\times10^{23}\times3.2}{32}$

= **6.022×10^{22} atoms.**

(*iii*) 180 g of glucose = 6.022×10^{23} molecules

18 g of glucose = $\frac{6.022\times10^{23}\times18}{180}$

= 6.022×10^{22} molecules

1 molecule of glucose = 6 + 12 + 6 = 24 atoms

6.022×10^{22} molecules of glucose

= $6.022 \times 10^{22} \times 24$ = **1.445×10^{24} atoms.**

(*iv*) 1 mole molecules of oxygen = 6.022×10^{23} molecules

0.20 mol molecules of oxygen = $6.022 \times 10^{23} \times 0.2$

= 1.2046×10^{23} molecules

1 molecule of oxygen = 2 atoms

1.2046×10^{23} molecules = $1.2046 \times 10^{23} \times 2$

= **2.409×10^{23} atoms.**

37. 40 g of calcium = 6.022×10^{23} atoms

15 g of calcium contain atoms

= $\frac{6.022\times10^{23}}{40} \times 15 = 2.258 \times 10^{23}$ atoms.

Now, number of sodium atoms = 2.258×10^{23}

6.022×10^{23} atoms of sodium has mass = 23 g

2.258×10^{23} atoms of sodium has mass

= $\frac{23}{6.022\times10^{23}} \times 2.258 \times 10^{23}$ = **8.624 g.**

38. (*i*) 28 g of nitrogen at N.T.P occupy volume = 22.4 L

1.4 g of nitrogen at N.T.P will occupy volume

= $\frac{22.4}{28} \times 1.4$ = **1.12 L.**

(*ii*) 6.022×10^{23} molecules of O_2 at N.T.P occupy volume = 22.4 L

6.022×10^{21} molecules of O_2 at N.T.P will occupy

volume = $\frac{22.4\times6.022\times10^{21}}{6.022\times10^{23}}$

= **0.224 L**

(*iii*) 1 mol of NH_3 occupy volume = 22.4 L

0.2 mol of NH_3 occupy volume = 22.4 × 0.2

= **4.48 L.**

39. Avogadro number of rupees = 6.022×10^{23} rupees

Rupees spent per second = 10^6

Rupees spent per year = $10^6 \times 60 \times 60 \times 24 \times 365$

∴ $10^6 \times 60 \times 60 \times 24 \times 365$ rupees are spent in = 1year

6.022×10^{23} rupees are spent in

= $\frac{1}{10^6\times60\times60\times24\times365} \times 6.022 \times 10^{23}$

= **1.91×10^{10} years.**

40. 1 gram atom corresponds to mass of 6.022×10^{23} atoms

Mass of 6.022×10^{23} atoms = $6.644 \times 10^{-23} \times 6.022 \times 10^{23}$

= 40.01 g

∴ 1 gram atom = 40.01 g

40.01 g of X = 1 gram atom

80×10^3 g of X = $\frac{1}{40.01} \times 80 \times 10^3$

= **1999.5 gram atoms.**

41. 22.4 L of ozone (O_3) at N.T.P = 6.022×10^{23} molecules

5.60 L of ozone at N.T.P = $\frac{6.022\times10^{23}}{22.4} \times 5.6$

= **1.506×10^{23} molecules.**

Now, 1 molecule of ozone = 3 atoms

1.506×10^{23} molecules of ozone = $1.506 \times 10^{23} \times 3$

= **4.518×10^{23} atoms.**

42. Gold present in 300 mg gold ring = $\frac{300\times20}{24}$

= 250 mg

Now, number of atoms present in 197 g

= 6.022×10^{23}

No. of atoms present in 250×10^{-3} g

= $\frac{6.022\times10^{23}\times250\times10^{-3}}{197}$

= **7.64×10^{20}.**

43. Molecular mass of KCl = 39 + 35.5 = 74.5 g

74.5 g of KCl = 1 mole atoms of K

1000 g of KCl = $\frac{1\times1000}{74.5}$ = 13.42 mole atoms of K

Now, molecular mass of K_2O = 39 × 2 + 16 = 94 g

2 mol atoms of K in K_2O weigh = 94 g

13.42 mol atoms of K in K_2O weigh = $\frac{94}{2} \times 13.42$

= 631 g = **0.631 kg.**

44. Gram molecular mass of $H_2C_2O_4.2H_2O$ = 126 g

No. of water molecules in 1 mol of oxalic acid = 2 mol

No. of water molecules in 126 g of oxalic acid = $2 \times 6.022 \times 10^{23}$

∴ No. of water molecules in 630×10^{-3} g of oxalic acid

= $\frac{2\times6.022\times10^{23}\times630\times10^{-3}}{126}$

= **6.022×10^{21}.**

45. Volume of CO_2 present in air = $1000 \times \frac{3}{100}$

= 0.03 mL

22400 ml of CO_2 at S.T.P. contain = 6.022×10^{23} molecules

0.3 mL of CO_2 at S.T.P. contain = $\frac{6.022\times10^{23}\times0.3}{22400}$

= **8.07×10^{18} molecules.**

46. Mass of dot = 10^{-6}

12 g of C contain atoms = 6.022×10^{23}

10^{-6} g of C contain atoms = $\frac{6.022\times10^{23}}{12} \times 10^{-6}$

= **5.019×10^{16} atoms.**

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47. 1 mol of CCl_4 = 154 g

154 g of CCl_4 contains $6.022 \times 10^{23} \times 4$ Cl atoms

or $6.022 \times 10^{23} \times 4$ Cl atoms are present in 154 g of CCl_4

1×10^{25} Cl atoms are present in $= \frac{154 \times 1 \times 10^{25}}{6.022 \times 10^{23} \times 4}$

$= 639.2$ g

Volume of $CCl_4 = \frac{\text{Mass}}{\text{Density}}$

$= \frac{639.2}{1.5} = 426$ cc

or $= \mathbf{0.426\ litre.}$

48. *Number of C atoms in 1.0 g of C-14 isotope*

14 g of C-14 isotope contains C atoms = 6.022×10^{23}

1 g C-14 isotope contain C atoms

$= \frac{6.022 \times 10^{23}}{14} \times 1$

$= 4.30 \times 10^{22}$

Number of C atoms in 1.0 of C-12 isotope

12 g of C-12 isotope contains C atoms $= 6.022 \times 10^{23}$

1g of C-12 isotope contain C atoms

$= \frac{6.022 \times 10^{23}}{12} \times 1$

$= 5.02 \times 10^{22}$

Difference in number of C atoms

$= 5.02 \times 10^{22} - 4.30 \times 10^{22}$

$= \mathbf{7.2 \times 10^{21}.}$

49. Molecular weight of $Na_2CO_3 . 10H_2O = 286$

Mass of oxygen present in $Na_2CO_3.10H_2O = 208$

Now 1 mol of $Na_2CO_3.10H_2O = 286$ g

0.1 mol of $Na_2CO_3.10H_2O = 28.6$ g

Wt. of oxygen present in 286 g of $Na_2CO_3 = 208$

Wt. of oxygen present in 28.6 g of $Na_2CO_3.10H_2O$

$= \frac{208}{286} \times 28.6$

$= \mathbf{20.8\ g.}$

50. (*i*) Molecular mass of $MgSO_4$

$= 24 + 32 + 4 \times 16 = 120$

Mass of Mg $= 24$

Mass percentage of Mg $= \frac{24}{120} \times 100 = \mathbf{20\%}$

Mass of S $= 32$

Mass percentage of S $= \frac{32}{120} \times 100 = \mathbf{26.67\%}$

Mass of O $= 4 \times 16 = 64$

Mass percentage of O $= \frac{64}{120} \times 100 = \mathbf{53.33\%.}$

(*ii*) Molar mass of $(NH_4)_2\ Cr_2O_7 = 2 \times (14 + 4) + 2 \times 52 + 7 \times 16 = 252$

No. of parts of cation $NH_4^+ = 2 \times (14 + 4) = 36$

Percentage of cation $= \frac{36}{252} \times 100 = \mathbf{14.29\ \%}$

51. (*i*) **Calculation of empirical formula**

Element	Percentage	Atomic mass	Moles of atoms	Atomic ratio	Simplest whole no. ratio
C	40.68	12	$\frac{40.68}{12} = 3.39$	$\frac{3.39}{3.39} = 1$	2
H	5.08	1	$\frac{5.08}{1} = 5.08$	$\frac{5.08}{3.39} = 1.50$	3
O	$100 - (40.68 + 5.08) = 54.24$	16	$\frac{54.24}{16} = 3.39$	$\frac{3.39}{3.39} = 1$	2

Empirical formula $= C_2H_3O_2$

Empirical formula mass $= 2 \times 12 + 3 \times 1 + 2 \times 16 = 59$

(*ii*) **Calculation of molecular formula**

Molecular mass $= 2 \times$ V.D. $= 2 \times 59 = 118$

$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{118}{59} = 2$

Molecular formula $= 2(C_2H_3O_2) = C_4H_6O_4.$

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o 52. (*i*) **Calculation of empirical formula**

Element	Percentage	Atomic mass	Mole ratio	Atomic ratio
C	54.2	12	$\frac{54.2}{12} = 4.50$	$\frac{4.50}{2.29} = 2$
H	9.2	1	$\frac{9.2}{1} = 9.2$	$\frac{9.2}{2.29} = 4$
O	36.6	16	$\frac{36.6}{16} = 2.29$	$\frac{2.29}{2.29} = 1$

Empirical formula = $\mathbf{C_2H_4O}$

(*ii*) **Calculation of molecular formula**

Empirical formula mass = $2 \times 12 + 4 \times 1 + 1 \times 16 = 44$

Molecular mass = 88

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{88}{44} = 2$$

$\therefore$ Molecular formula = $2(C_2H_4O) = \mathbf{C_4H_8O_2}$.

o 53. (*i*) **Calculation of empirical formula**

Element	Percentage	Moles of atoms	Atomic ratio	Simplest ratio
N	30.43	14	$\frac{30.43}{14} = 2.17$	$\frac{2.17}{2.17} = 1$
O	69.57	16	$\frac{69.57}{16} = 4.35$	$\frac{4.35}{2.17} = 2$

Empirical formula = $\mathbf{NO_2}$

(*ii*) **Calculation of molecular formula**

Empirical formula mass = $14 + 2 \times 16 = 46$

Molecular mass = 92

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{92}{46} = 2$$

Molecular formula = $2\ (NO_2) = \mathbf{N_2O_4}$.

o 54. (*i*) **Calculation of empirical formula**

Element	Percentage	Atomic mass	Moles of atoms	Simplest ratio
Na	36.5	23	$\frac{36.5}{23} = 1.59$	$\frac{1.59}{0.79} = 2$
H	0.8	1	$\frac{0.8}{1} = 0.8$	$\frac{0.8}{0.79} = 1$
P	24.6	31	$\frac{24.6}{31} = 0.79$	$\frac{0.79}{0.79} = 1$
O	38.1	16	$\frac{38.1}{16} = 2.38$	$\frac{2.38}{0.79} = 3$

Empirical formula = $\mathbf{Na_2HPO_3}$

(*ii*) **Calculation of molecular formula**

Empirical formula mass = $2 \times 23 + 1 \times 1 + 1 \times 31 + 3 \times 16 = 126$

Molecular mass = 126

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$$n = \frac{126}{126} = 1$$

Molecular formula = Na_2HPO_3 **Name : Sodium hydrogen phosphite.**

o 55. (*i*) **Calculation of empirical formula**

Element	Percentage	Atomic mass	Atomic ratio	Simple atomic ratio
Mg	20.0	24	$\frac{20.0}{24} = 0.83$	$\frac{0.83}{0.83} = 1$
S	26.66	32	$\frac{26.66}{32} = 0.83$	$\frac{0.83}{0.83} = 1$
O	53.33	16	$\frac{53.33}{16} = 3.33$	$\frac{3.33}{0.83} = 4$

Empirical formula = $MgSO_4$

(*ii*) **Calculation of molecular formula**

Empirical formula mass = 24 + 32 + 4 x 16 = 120

Molecular mass = 120

$$n = \frac{120}{120} = 1$$

Molecular formula of anhydrous salt = $MgSO_4$

Let molecular formula mass = 100

Loss of weight due to dehydration = 51.2%

Molecular mass of anhydrous salt = 100 – 51.2 = 48.8

Now, if molecular mass of anhydrous salt is 48.8, then that of hydrated salt is = 100

If molecular mass of anhydrous salt is 120, then that of hydrated salt is = $\frac{100}{48.8} \times 120 = 245.9$

Loss in weight due to dehydration = 245.9 – 120 = 125.9

No. of water molecules in hydrated sample = $\frac{125.9}{18} = 7$

Molecular formula of hydrated salt (crystalline salt) = $MgSO_4 . 7H_2O$.

o 56.

Compound	Percentage	Molecular formula mass	Relative no.	Simple ratio	Simplest whole no. ratio
CuO	44.82	79.5	$\frac{44.82}{79.5} = 0.564$	$\frac{0.564}{0.564} = 1$	1
SiO_2	34.83	60	$\frac{34.83}{60} = 0.580$	$\frac{0.580}{0.564} = 1.03$	1
H_2O	20.35	18	$\frac{20.35}{18} = 1.12$	$\frac{1.12}{0.564} = 2.0$	2

Empirical formula = $CuO . SiO_2 . 2H_2O$.

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57.

Element / Compound	Percentage	At. mass/ Molecular mass	Relative no.	Simple ratio	Simplest whole no. ratio
Fe	20	56	$\frac{20}{56} = 0.36$	$\frac{0.36}{0.36} = 1$	1
S	11.5	32	$\frac{11.5}{32} = 0.36$	$\frac{0.36}{0.36} = 1$	1
O	23.1	16	$\frac{23.1}{16} = 1.44$	$\frac{1.44}{0.36} = 4$	4
H_2O	45.4	18	$\frac{45.4}{18} = 2.52$	$\frac{2.52}{0.36} = 7$	7

Empirical formula = **$FeSO_4 . 7H_2O$.**

60. $Fe_2O_3 + 3H_2 \longrightarrow 2Fe + 3H_2O$

$2 \times 56 + 3 \times 16 = 160$ (1 kg); $2 \times 56 = 112$ (?)

160 g of Fe_2O_3 on reduction gives iron = 112 g

1000 g of Fe_2O_3 on reduction will give iron

$$= \frac{112}{160} \times 1000 = 700 \text{ g}$$

$$= \textbf{0.7 kg.}$$

61. $C_{12}H_{22}O_{11} + 12O_2 \longrightarrow 12CO_2 + 11H_2O$

342g; 34×24 g; 12×32g; ?

Energy requirement in a day = 34×24 g of sucrose

Amount of oxygen needed for burning 342 g of sucrose = 12×32 g

Amount of oxygen needed for burning 34×24 g of sucrose

$$= \frac{12 \times 32}{342} \times 34 \times 24$$

$$= \textbf{916.2 g.}$$

62. $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$

100 g; 22.4 L at N.T.P.

22.4 L of CO_2 at N.T.P. is obtained from $CaCO_3$

$$= 100 \text{ g}$$

100 L of CO_2 at N.T.P. will be obtained from $CaCO_3$

$$= \frac{100}{22.4} \times 100 = 446.4 \text{ g}$$

Impure marble required $= \frac{446.4 \times 100}{96.5} = \textbf{462.6 g.}$

63. $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

22.4 L; 5.6 L; 1mol; ?

22.4 L of methane on ignition give = 1 mol of CO_2

5.6 L of methane on ignition will give CO_2

$$= \frac{1}{22.4} \times 5.6 = \textbf{0.25 mol.}$$

64. Let us first calculate the theoretical yield of BI_3

$NaBH_4 + 4I_2 \longrightarrow BI_3 + NaI + 4HI$

$23+10.8 + 4 \times 1 = 37.8$ g; $10.8 + 3 \times 127 = 391.8$ g

37.8 g of $NaBH_4$ give BI_3 = 391.8 g

64 g of $NaBH_4$ will give $BI_3 = \frac{391.8}{37.8} \times 64 = 663.36$ g

Experimental yield = 15.0 g

$$\text{Percentage yield} = \frac{15.0 \times 100}{663.36}$$

$$= \textbf{2.27\%.}$$

65. $5KNO_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow$

$5(39 + 14 + 2 \times 16) = 425$ g; $2(39 + 54.9 \times 4 \times 16) = 315.8$ g

$5KNO_3 + 2MnSO_4 + K_2SO_4 + 3H_2O$

For oxidising 425 g of KNO_2, $KMnO_4$ needed

$$= 315.8 \text{ g}$$

For oxidising 11.4 g of KNO_2, $KMnO_4$ will be needed

$$= \frac{315.8}{425} \times 11.4$$

$$= \textbf{8.47 g.}$$

66. $2KMnO_4 + 8H_2SO_4 + 10KI \longrightarrow$

$2(39 + 54.9 + 4 \times 16) = 315.8$ g; $10(39.5 + 127) = 1665$ g

$6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$

1665 g of KI require for conversion to I_2 = 315.8 g $KMnO_4$

75 g of KI will require for conversion to I_2

$$= \frac{315.8 \times 75}{1665} = \textbf{14.22 g}$$

158 g of $KMnO_4$ is present in = 1000 mL

14.23 g of $KMnO_4$ will be present in

$$= \frac{1000}{158} \times 14.22 = \textbf{90.05 mL.}$$

67. Mass of NaOH = 0.38 g

$$\text{Moles of NaOH} = \frac{0.38}{40}$$

Volume of solution = 50.0 mL

$$\text{Molarity} = \frac{0.38/40}{50.0} \times 1000$$

$$= \textbf{0.19 M.}$$

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68. 3 molal solution of NaOH means that 3 mol of NaOH are present in 1000 g of solvent.

Mass of 3 mol of NaOH = $3 \times 40 = 120$ g

Mass of solution = $1000 + 120 = 1120$ g

$$\text{Volume of solution} = \frac{1120\,\text{g}}{1.110\,\text{g mL}^{-1}}$$

$$= 1009.0\ \text{mL}$$

$$\text{Molarity} = \frac{3}{1009.0} \times 1000$$

$$= \mathbf{2.97\ M}$$

69. $M_1V_1 = M_2V_2$

$$2.4 \times 500 = 1.6 \times V_2$$

or $$V_2 = \frac{2.4 \times 500}{1.6} = 750\ \text{ml}$$

Volume of water to be added = $750 - 500 = \mathbf{250\ mL}$.

70. 86% by weight of H_2SO_4 means that 86 g of H_2SO_4 is present in 100 g of solution

$$\text{Volume of 100 g solution} = \frac{100}{1.80} = 55.6\ \text{ml}$$

$$\text{Moles of } H_2SO_4 = \frac{86}{98}$$

$$\text{Molarity} = \frac{86/98}{55.6} \times 1000$$

$$= \mathbf{15.8\ M.}$$

71. Molecular mass of $(COOH)_2.2H_2O = 126$

$$\text{Moles of oxalic acid} = \frac{0.63}{126} = 0.005\ \text{mol}$$

$$\text{Molarity} = \frac{0.005}{500} \times 1000$$

$$= \mathbf{0.01\ M.}$$

72. $$\text{Molarity} = \frac{\text{Moles of NaOH}}{\text{Vol. of solution}} \times 1000$$

Molarity = 0.15 M, vol. of solution = 27 mL

$$\therefore \quad 0.15 = \frac{\text{Moles of NaOH}}{27} \times 1000$$

$$\therefore \text{ Moles of NaOH} = \frac{27 \times 0.15}{1000}$$

$$= \mathbf{0.00405\ mol}.$$

73. $$\text{Moles of oxalic acid} = \frac{\text{Molarity} \times \text{Volume in mL}}{1000}$$

$$\text{Moles of oxalic acid} = \frac{0.01 \times 100}{1000} = 0.001$$

1 mole of oxalic acid = 6.022×10^{23} molecules

0.001 mole of oxalic acid = $6.022 \times 10^{23} \times 0.001$

$$= \mathbf{6.022 \times 10^{20}.}$$

74. $AgNO_3 + HCl \longrightarrow AgCl + HNO_3$

1000 mL of 0.068 M $AgNO_3$ contain $AgNO_3$

= 0.068 mol

25 mL of 0.068 $AgNO_3$ contain $AgNO_3$

$$= \frac{0.068}{1000} \times 25$$

$$= 0.0017\ \text{mol}$$

1 mol of $AgNO_3$ give 1 mol of AgCl and therefore, 0.0017 mol of $AgNO_3$ will form 0.0017 mol of AgCl,

Amount of AgCl obtained = 0.0017×143.5

$$= \mathbf{0.244\ g}.$$

75. $2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$

1000 mL of 0.15 M H_2SO_4 contain = 0.15 mol

20 mL of 0.15M H_2SO_4 contain

$$= \frac{0.15}{1000} \times 20$$

$$= 0.003\ \text{mol}$$

According to equation, 2 mol of KOH react with 1 mol of H_2SO_4 so that 0.003 mol of H_2SO_4 will react with $2 \times 0.003 = 0.006$ mol of KOH

0.34 mol of 0.34 M KOH are present in = 1000 mL

0.006 mol of 0.34 M KOH are present in

$$= \frac{1000}{0.34} \times 0.006$$

$$= \mathbf{17.65\ mL.}$$

76. $NaOH\,(aq) + HCl\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)$

1000 mL of 2.0 mol L^{-1} contain NaOH = 2.0 mol

200 mL of 2.0 mol L^{-1} contain NaOH

$$= \frac{2.0}{1000} \times 200$$

$$= 0.4\ \text{mol}$$

1 mol of NaOH is neutralised by 1 mol of HCl

0.4 mol of NaOH will be neutralised by 0.4 mol of HCl

1.0 mol of 1.0 mol L^{-1} is present in 1000 mL

0.4 mol of 1.0 mol L^{-1} is present in $\frac{1000}{1.0} \times 0.4$

$$= \mathbf{400\ mL}$$

1 mol of NaOH on reaction with HCl give = 58.5 g NaCl

0.4 mol of NaOH on reaction with HCl will give

$$= \frac{58.5}{1} \times 0.4$$

$$= \mathbf{23.4\ g.}$$

77. Molecular mass of NaOH = 23 + 16 + 1 = 40

1 M solution of NaOH contains 40 g L^{-1}

0.150 M solution of NaOH contains 4.0×0.150

$$= 6\ \text{g L}^{-1}$$

6 g of NaOH is present in 1000 mL

0.184 g of NaOH is present in

$$= \frac{1000 \times 0.184}{6}$$

$$= \mathbf{30.7\ mL\ of\ NaOH.}$$

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78. $BaCl_2\,(aq) + Na_2SO_4\,(aq) \longrightarrow BaSO_4\,(s) + 2NaCl$

1000 mL of 0.250 M Na_2SO_4 contain Na_2SO_4
$= 0.250$ mol

500 mL of 0.250 M Na_2SO_4 cantain Na_2SO_4

$$= \frac{0.250}{1000} \times 500 = 0.125 \text{ mol}$$

$$\text{Moles of } BaCl_2 = \frac{15}{208} = 0.0721 \text{ mol}$$

$\therefore$ $BaCl_2$ is limiting reactant.

Molecular mass of $BaSO_4 = 233$

1 mol of $BaCl_2$ react with Na_2SO_4 to give
$= 233$ g $BaSO_4$

0.072 mol of $BaCl_2$ will react with Na_2SO_4 to give
$= 233 \times 0.072 =$ **16.78 g.**

79. The balanced chemical equation is :

$CaCO_3\,(s) + 2\,HCl\,(aq) \longrightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)$

Let us first calculate the moles of HCl in 25 mL of 0.75 M HCl

1000 mL of 0.75 M HCl contain HCl $= 0.75$ mol

$$25 \text{ mL of } 0.75 \text{ M HCl contain HCl} = \frac{0.75}{1000} \times 25$$

$$= 0.01875 \text{ mol}$$

2 mol of HCl completely react with 1 mol of $CaCO_3$

0.01875 mol of HCl will completely react with

$$= \frac{1}{2} \times 0.01875$$

$= 0.009375$ mol

Mass of 0.009375 mol of $CaCO_3 = 0.009375 \times 100$
$=$ **0.9375 g**

Chapter Summary

Key Terms & Laws

- **Precision** refers for the closeness of the set of values obtained from identical measurements of a quantity.
- **Accuracy** refers to the closeness of a single measurement to its true value.
- All numbers, small or large are expressed as a number between 1.000 ..... and 9.999 multiplied or divided by 10, an appropriate number of times.
  $\Rightarrow 1426.2 = 1.4262 \times 10^3$
  In **scientific notation,** a number is generally expressed in the form $N \times 10^n$
  where N is a number (called digit term) between 1.000 ..... and 9.999 and n is a number called an exponent.
- The **significant figures** in a number are all the certain digits plus one doubtful digit.
- In **addition and subtraction,** the final result should be reported to the same number of decimal places as the number with the minimum number of decimal places.
- In **multiplication and division,** the final result should be reported as having the same number of significant digits as the number with least number of significant digits.
- **Law of conservation of mass (Lavoisier in 1774).** During any physical or chemical change, the total mass of the products formed is equal to the total mass of reactants consumed.
- **Law of constant composition (Proust in 1798).** A chemical compound always contains same elements combined together in same proportion by mass.
- **Law of multiple proportions (John Dalton in 1803).** When two elements combine together to form two or more than two compounds then the masses of one of the elements that combine with fixed mass of the other bear a simple whole number ratio to one another.
- **Law of reciprocal proportions (Richter in 1792).** When two different elements combine separately with a fixed mass of a third element, then the ratio of their masses in which they do so is either the same or some whole number multiple of the ratio in which they combine with each other.
- **Gay Lussac's law (Gay Lussac in 1808).** When gases react with each other they do so in volumes which bear a simple whole number ratio to one another and to the volume of the products, if they are also gases, provided all volumes are measured under similar condition of temperature and pressure.
- **Avogadro's law.** Equal volume of all gases under similar conditions of temperature and pressure contain equal number of molecules.
- The smallest particle of an element that takes part in chemical reactions is **atom.**
- The smallest particle of a substance that has independent existence is **molecule.**
- One twelveth (1/12) of the mass of an atom of carbon (C-12) is **atomic mass unit.** It is equal to 1.66×10^{-27} kg.
- **Atomic mass** is the average relative mass of an atom of element as compared with mass of a carbon atom (C-12) taken as 12 a.m.u.
- **Molecular mass** is the average relative mass of a molecule of the substance as compared with mass of a carbon atom (C-12) taken as 12 a.m.u.
- Atomic mass expressed in grams is **gram atomic mass** and molecular mass expressed in grams is **gram molecular mass.**
- **One mole** is 6.022×10^{23} specified particles.

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- Volume occupied by one mole of a gaseous substance is called gram molecular volume (G.M.V.). Its value is 22.4 L at N.T.P.
- **Mass percentage composition** of a compound gives the mass of each element expressed as percentage of the total mass.
- **Empirical formula** is the formula which gives the simplest whole number ratio of atoms of different elements present in the molecule of a compound.
  Molecular formula is the formula which gives the actual number of atoms present in the molecule of the compound. It is whole number multiple of empirical formula.
- **Molarity** is the number of moles of solute dissolved per litre of solution. It is expressed as mol dm^{-3} or M.
  Molarity changes with temperature because volume of the solution changes with temperature.
- **Limiting reactant** is the reactant which is completely consumed in the reaction.

QUICK CHAPTER ROUND UP

Matter
anything which occupies space and has mass.

Physical classification

- **solids.** definite shape and definite volume
- **liquids.** definite volume but no definite shape
- **gases.** neither definite shape nor definite volume

$$\text{solid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{liquid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{gas}$$

Chemical classification

Pure substances

- **Element:** simplest form of matter
- **Compound:** contain more than one kind of elements combined in a definite proportion

Mixtures

- **Homogeneous:** Uniform composition throughout
- **Heterogeneous:** composition is not uniform throughout

- The **significant figures** in a number are all the certain digits plus one doubtful digit.
- In **addition and subtraction**, the final result should be reported to the same number of decimal places as the number with the minimum number of decimal places.
- In **multiplication and division**, the final result should be reported as having the same number of significant digits as the number with least number of significant digits.

Smallest particle of element which may or may not have independent existence ⇒ **atom.**
Smallest particle of a substance (element or compound) which has independent existence ⇒ **molecule**

$$1 \text{ MOLE} = 1.6022 \times 10^{23} \text{ particles}$$

6.022×10^{23} particles ⟷ 1 MOLE ⟷ 22.4 L of a gas at N.T.P.

1 MOLE → 1 gram atom of an element; 1 MOLE → 1 gram molecule of a substance

$$\text{Atomic mass} = \frac{\text{Mass of an atom}}{\frac{1}{12}\text{th mass of } {}^{12}C}$$

$$\text{Molecular mass} = \frac{\text{Mass of a molecule}}{\frac{1}{12}\text{th mass of } {}^{12}C}$$

- One twelveth (1/12) of the mass of an atom of carbon (C-12) is atomic mass unit. It is equal to 1.66×10^{-27} kg.

$$\text{One mole of atoms} = 6.022 \times 10^{23} \text{ atoms} = \text{Gram atomic mass of the element}$$

$$\text{Moles of an element} = \frac{\text{Mass of element}}{\text{Atomic mass}}$$

$$\text{Mass of one atom} = \frac{\text{Atomic mass}}{6.022 \times 10^{23}}$$

$$\text{One mole of molecules} = 6.022 \times 10^{23} \text{ molecules} = \text{Gram molecular mass}$$

$$\text{Moles of a compound} = \frac{\text{Mass of compound}}{\text{Molar mass}}$$

$$\text{Mass of one molecule} = \frac{\text{Molecular mass}}{6.022 \times 10^{23}}$$

Volume occupied by 1 mole of a gas at N.T.P. = 22.4 L

- Atomic mass expressed in grams is **gram atomic mass** or **gram atom** and molecular mass expressed in grams is **gram molecular mass** or **gram molecule**.

- **Mass percentage composition** of a compound gives the mass of each element expressed as percentage of the total mass.

$$\text{Mass \% of an element} = \frac{\text{Mass of element in 1 mole of compound}}{\text{Molar mass}} \times 100$$

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- The formula which gives the simplest whole number ratio of atoms of different elements present in the molecule of a compound is **empirical formula**.
- The **molecular formula** gives the actual number of atoms present in the molecule of the compound. It is whole number multiple of empirical formula.
- Molecular formula = n (Empirical formula)

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

Molarity equation :

$$M_1V_1 = M_2V_2$$

$$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Vol. of solution (in mL)}} \times 1000$$

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in g)}} \times 1000$$

$$\text{Normality (N)} = \frac{\text{Gram equiv. of solute}}{\text{Vol. of solution (in mL)}} \times 1000$$

$$\text{Normality} = \text{Molarity} \times \frac{\text{Mol. mass}}{\text{Eq. mass}}$$

$$\text{Mole fraction of solute}(x_B) = \frac{\text{Moles of solute}}{\text{Moles of solute + Moles of solvent}}$$

Mole fraction of solute + Mole fraction of solvent = 1

or Mole fraction of solvent=1 – Mole fraction of solute.

Limiting reactant ▸ the reactant which reacts completely in a reation.

NCERT FILE Solved

NCERT Textbook Exercises

Q. 1. Calculate the molecular mass of the following:

(*i*) H_2O (*ii*) CO_2 (*iii*) CH_4

Ans. (*i*) Molecular mass of H_2O

= 2 (1.008 u) + (16.00 u) = 18.016 u

(*ii*) Molecular mass of CO_2

= 1 (12.01 u) + 2(16.00 u) = 44.01 u

(*iii*) Molecular mass of CH_4

= 1 (12.01 u) + 4(1.008 u) = 16.042u

Q. 2. Calculate the mass percent of different elements present in sodium sulphate (Na_2SO_4).

Ans. Molar mass of Na_2SO_4

= 2 × At. mass of Na + At. mass of S + 4 × At. mass of O

= 2 × 23.0 + 32 + 4 × 16 = 142

$$\text{Mass \% of sodium} = \frac{2\times23}{142} \times 100 = 32.39\%$$

$$\text{Mass \% of sulphur} = \frac{32}{142} \times 100 = 22.53\%$$

$$\text{Mass \% of oxygen} = \frac{4\times16}{142} \times 100 = \mathbf{45.07\%}$$

Q. 3. Determine the empirical formula of an oxide of iron which has 69.9% iron and 30.1% dioxygen by mass. (Atomic masses : Fe = 55.85 amu, O = 16.00 amu).

Ans. *Refer Solved Example 63 (Page 53).*

Q. 4. Calculate the amount of carbon dioxide that would be produced when

(*i*) 1 mole of carbon is burnt in air

(*ii*) 1 mole of carbon is burnt in 16 g of dioxygen

(*iii*) 2 moles of carbon are burnt in 16 g of dioxygen

Ans. The balanced chemical equation of combustion of carbon in dioxygen (or air) is

$$\underset{1\text{ mol}}{C(s)} + \underset{1\text{ mol}}{O_2(g)} \longrightarrow \underset{1\text{ mol}}{CO_2(g)}$$

(*i*) In air, carbon will be completely burnt. 1 mol of carbon will give 1 mol of CO_2 or = 44g

(*ii*) Since only 16 g of dioxygen is available (0.5 mol), it will combine with only 0.5 mol of carbon. Dioxygen is the limiting reagent. Thus, 0.5 mol of carbon will be burnt to give 0.5 mol of CO_2 or = 22 g

(*iii*) In this case also, dioxygen is limiting reagent and only 0.5 mol of carbon will be burnt. It will produce 22 g of CO_2.

Q. 5. Calculate the mass of sodium acetate (CH_3COONa) required to make 500 mL of 0.375 molar aqueous solution. Molar mass of sodium acetate is 82.0245 g mol^{-1}.

Ans. 0.375 M aqueous solution means that 0.375 mol of sodium acetate are present in 1000 mL of solution. 500 mL of the solution should contain sodium acetate

$$= \frac{0.375}{2} \text{ mol}$$

Molar mass of sodium acetate = 82.0245 g mol^{-1}

$$\text{Mass of sodium acetate required} = \frac{0.375}{2} \times 82.0245$$

$$= \mathbf{15.38\ g}$$

Alternatively, it may be solved as :

$$\text{Molarity} = \frac{\dfrac{\text{Mass of sodium acetate}}{\text{Molar mass}}}{\text{Volume}} \times 1000$$

$$0.375 = \frac{\dfrac{\text{Mass of sodium acetate}}{82.0245}}{500} \times 1000$$

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$$\therefore \text{ Mass of sodium acetate} = \frac{0.375 \times 82.0245 \times 500}{1000}$$

$$= 15.38 \text{ g}$$

Q. 6. Calculate the concentration of nitric acid in moles per litre in a sample which has a density, 1.41 g mL^{-1} and the mass per cent of nitric acid in it being 69%.

Ans. *Refer Solved Example 101 (Page 69).*

Q. 7. How much copper can be obtained from 100 g of copper sulphate ($CuSO_4$) ? (Atomic mass of Cu = 63.5 amu).

Ans. 1 mol of $CuSO_4$ contains 1 mol (1 gram atom) of Cu

Molar mass of $CuSO_4 = 63.5 + 32 + 4 \times 16$

$= 159.5\ g$

$\therefore$ 159.5 g of $CuSO_4$ will give Cu = 63.5 g

$$100 \text{ g of } CuSO_4 \text{ will give Cu} = \frac{63.5}{159.5} \times 100$$

$$= 39.81 \text{ g}$$

Q. 8. Determine the molecular formula of an oxide of iron in which the mass per cent of iron and oxygen are 69.9 and 30.1 respectively. Given that the molecular mass of iron oxide is 159.8 and atomic masses : Fe = 55.85 amu and O = 16.00 amu.

Ans. Calculation of empirical formula = Fe_2O_3 (See Solved Example 65)

Empirical formula mass of Fe_2O_3

$= 2 \times 55.85 + 3 \times 16.00$

$= 111.7 + 48.00 = 159.7 \text{ g mol}^{-1}$

Molecular formula mass = 159.8 g mol^{-1}

$$n = \frac{\text{Molecular formula mass}}{\text{Empirical formula mass}}$$

$$= \frac{159.8}{159.7} = 1$$

$\therefore$ Molecular formula = $(Fe_2O_3) = Fe_2O_3$

Q. 9. Calculate the atomic mass (average) of chlorine using the following data :

	% Natural abundance	Molar mass
^{35}Cl	75.77	34.9689
^{37}Cl	24.23	36.9659

Ans. Average atomic mass of Cl

$$= \frac{75.77 \times 34.9689 + 24.23 \times 36.9659}{100}$$

$$= 35.453$$

Q. 10. In three moles of ethane (C_2H_6), calculate the following :

(*i*) Number of moles of carbon atoms

(*ii*) Number of moles of hydrogen atoms

(*iii*) Number of molecules of ethane

Ans. (*i*) 1 mole of C_2H_6 contains 2 moles of carbon

$\therefore$ Number of moles of carbon in 3 moles of $C_2H_6 = 6$

(*ii*) 1 mole of C_2H_6 contain 6 mole atoms of hydrogen

$\therefore$ Number of moles of hydrogen atoms in 3 moles of $C_2H_6 = 3 \times 6 = 18$

(*iii*) 1 mole of $C_2H_6 = 6.022 \times 10^{23}$ molecules

$\therefore$ Number of molecules in 3 moles of $C_2H_6 = 3 \times 6.022 \times 10^{23}$

$= 1.807 \times 10^{24}$ **molecules**

Q. 11. What is the concentration of sugar ($C_{12}H_{22}O_{11}$) in mol L^{-1} if its 20g are dissolved in enough water to make a final volume upto 2 L ?

Ans. *Refer Solved Example 103 (Page 70).*

Q. 12. If the density of methanol is 0.793 kg L^{-1}, what is its volume needed for making 2.5 L of its 0.25 M solution ?

Ans. *Refer Solved Example 104 (Page 70).*

Q. 13. Pressure is defined as force per unit area of the surface. The SI unit of pressure, pascal is shown below :

$$1 \text{ Pa} = 1 \text{Nm}^{-2}$$

If mass of air at sea level is 1034 g cm^{-2}, calculate the pressure in pascal.

Ans. Pressure is force (i.e., weight) acting per unit area

But weight = mg

$\therefore$ Pressure = Weight per unit area

$$= \frac{1034 \text{g}}{\text{cm}^2} \times 9.8 \text{ ms}^{-2}$$

$$= \frac{1034 \text{ g}}{\text{cm}^2} \times 9.8 \text{ ms}^{-2} \times \frac{1 \text{ kg}}{1000 \text{ g}}$$

$$\times \frac{100 \text{ cm} \times 100 \text{ cm}}{1 \text{ m} \times 1 \text{ m}} \times \frac{1 \text{N}}{\text{kg m s}^{-2}} \times \frac{1 \text{Pa}}{1 \text{Nm}^{-2}}$$

$= 1.01332 \times 10^5$ **Pa**

Q. 14. What is the SI unit of mass ? How is it defined?

Ans. The SI unit of mass is kilogram (kg). Kilogram is defined as the mass of platinum-iridium (Pt-Ir) block, stored at the International Bureau of Weights and Measures in France. Thus it is the mass of the international prototype of the kilogram.

Q. 15. Match the following prefixes with their multiples :

	Prefixes	Multiples
(*i*)	**micro**	10^6
(*ii*)	**deca**	10^9
(*iii*)	**mega**	10^{-6}
(*iv*)	**giga**	10^{-15}
(*v*)	**femto**	**10**

Ans. (*i*) micro – 10^{-6} (*ii*) deca – 10 (*iii*) mega –10^6 (*iv*) giga – 10^9 (*v*) femto – 10^{-15}

Q. 16. What do you mean by significant figures ?

Ans. The significant figures in a number are all the certain digits plus one doubtful digit. It depends upon the precision of the scale or instrument used for the measurement. For example, if volume of a liquid is reported to be 18.25 mL, the digits 1, 8 and 2 are certain while 5 is doubtful. So, it has four significant figures (three certain plus one doubtful).

Q. 17. A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$, supposed to be carcinogenic in nature. The level of contamination was 15 ppm (by mass).

(*i*) Express this in per cent by mass.

(*ii*) Determine the molality of chloroform in the water sample.

Ans. (*i*) 15 ppm means that 15 parts of chloroform is present in 10^6 parts.

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$\therefore$ % by mass of $CHCl_3$ = $\frac{15}{10^6} \times 100 = 1.5 \times 10^{-3}\%$

(*ii*) Molar mass of $CHCl_3$ = $12 + 1 + 3 \times 35.5 = 119.5$

Moles of $CHCl_3$ = $\frac{1.5 \times 10^{-3}\,g}{119.5\,g\ mol^{-1}}$

$= 1.255 \times 10^{-5}$

Mass of water = 100 g

$\therefore$ Molality = $\frac{1.225 \times 10^{-5}}{100} \times 1000$

$= \mathbf{1.255 \times 10^{-4}\ m}$

Q. 18. Express the following in the scientific notation.

(*i*) 0.0048 (*ii*) 234,000 (*iii*) 8008

(*iv*) 500.0 (*v*) 6.0012

Ans. *Refer Solved Example 2 (Page 15).*

Q.19. How many significant figures are present in the following ?

(*i*) 0.0025 (*ii*) 208 (*iii*) 5005

(*iv*) 126,000 (*v*) 500.0 (*vi*) 2.0034

Ans. (*i*) 2 (*ii*) 3 (*iii*) 4

(*iv*) 3 (*v*) 4 (*vi*) 5

Q. 20. Round up the following upto three significant figures :

(*i*) 34.216 (*ii*) 10.4107 (*iii*) 0.04597 (*iv*) 2808

Ans. (*i*) 34.2 (*ii*) 10.4 (*iii*) 0.0460 (*iv*) 2810

Q. 21. The following data were obtained when dinitrogen and dioxygen react together to form different compounds :

	Mass of dinitrogen	Mass of dioxygen
(*i*)	14 g	16 g
(*ii*)	14 g	32 g
(*iii*)	28 g	32 g
(*iv*)	28 g	80 g

(*a*) Which law of chemical combination is obeyed by the above experimental data ? Give its statement.

(*b*) Fill in the blanks in the following conversions :

(*i*) 1 km = ... mm = ... pm

(*ii*) 1 mg = ... kg = ... ng

(*iii*) 1 mL = ... L = ... dm^3

Ans. **(*a*)** Fixing the mass of dinitrogen as 14 g, the masses of dioxygen combined will be

16 : 32 : 16 : 40

or 2 : 4 : 2 : 5

This is a simple whole number ratio and hence, the data illustrate the **law of multiple proportions**. The law of multiple proportions states that when two elements combine to form two or more than two compounds, then the mass of one of the elements which combine with a fixed mass of the other bear a simple whole number ratio.

(*b*) (*i*)

$1\ km = 1\ km \times \frac{1000\,m}{1\,km} \times \frac{100\,cm}{1\,m} \times \frac{10\,mm}{1\,cm} = 10^6 mm$

$1\ km = 1\ km \times \frac{1000\,m}{1\,km} \times \frac{1\,pm}{10^{-12}\,m} = 10^{15}\ pm$

Correct answer : 10^6, 10^{15}

(*ii*) $1mg = 1mg \times \frac{1\,g}{1000\,mg} \times \frac{1\,kg}{1000\,g} = 10^{-6}\ kg$

$1\ mg = 1\ mg \times \frac{1\,g}{1000\,mg} \times \frac{1\,ng}{10^{-9}\,g} = 10^6\ ng$

Correct answer : 10^{-6}, 10^6

(*iii*) $1\ mL = 1mL \times \frac{1\,L}{1000\,mL} = 10^{-3}\ L$

$1\ mL = 1\ cm^3 \times \left(\frac{1\,dm}{10\,cm}\right)^3 = 10^{-3}\ dm^3$

Correct answer : 10^{-3}, 10^{-3}

Q. 22. If the speed of light is $3.0 \times 10^8\ ms^{-1}$, calculate the distance covered by light in 2.00 ns.

Ans. Distance covered by light = Speed × Time

$= 3.0 \times 10^8\ ms^{-1} \times 2.00\ ns \times \left(\frac{10^{-9}}{1ns}\right)$

$= 6.00 \times 10^{-1}\ m = \mathbf{0.600\ m}$

Q. 23. In a reaction

$A + B_2 \longrightarrow AB_2$

identify the limiting reagent if any in the following reaction mixtures :

(*i*) 300 atoms of A + 200 molecules of B

(*ii*) 2 mol of A + 3 mol of B

(*iii*) 100 atoms of A + 100 molecules of B

(*iv*) 5 mol of A + 2.5 mol of B

(*v*) 2.5 mol of A + 5 mol of B

Ans. *Refer Solved Example 88 (Page 65).*

Q. 24. Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation :

$N_2\ (g) + 3H_2\ (g) \longrightarrow 2NH_3\ (g)$

(*i*) Calculate the mass of ammonia produced if 2.00×10^3 g of dinitrogen reacts with 1.00×10^3g of dihydrogen.

(*ii*) Will any of the two reactants remain unreacted ?

(*iii*) If yes, which one and what would be its mass ?

Ans. *Refer Solved Example 92 (Page 66).*

Q. 25. How are 0.50 m Na_2CO_3 and 0.50 M Na_2CO_3 different ?

Ans. Molar mass of $Na_2CO_3 = 2 \times 23 + 12 + 3 \times 16$

$= 106\ g\ mol^{-1}$

Mass of 0.5 mol of $Na_2CO_3 = 106 \times 0.5 = 53$ g

0.50 m Na_2CO_3 solution means that 0.5 mol or 53g of Na_2CO_3 are present in 1000 g of solvent.

0.50 M Na_2CO_3 solution means that 0.5 mol or 53 g of Na_2CO_3 are present in 1 L of the solution.

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Q. 26. If ten volumes of dihydrogen gas react with five volumes of dioxygen gas, how many volumes of water would be produced ?

Ans. Dihydrogen (H_2) reacts with dioxygen (O_2) as

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(g)$$

2 volumes of dihydrogen react with 1 volume of O_2 to produce 2 volumes of water vapour. Thus,

10 volumes of dihydrogen will react completely with 5 volumes of dioxygen to produce 10 volumes of water.

10 volumes of water would be produced.

Q. 27. Convert the following into basic units :
(i) 28.7 pm (ii) 15.15 μs (iii) 25365 mg

Ans. (*i*) $28.7\text{ pm} = 28.7\text{ pm} \times \frac{10^{-12}\text{m}}{1\text{pm}} = 2.87 \times 10^{-11}\text{ m}$

(*ii*) $15.15\ \mu\text{s} = 15.15\ \mu\text{s} \times \frac{10^{-6}\text{s}}{1\mu\text{s}} = 1.515 \times 10^{-5}\text{ s}$

(*iii*) $25365\text{ mg} = 25365\text{ mg} \times \frac{1\text{g}}{1000\text{ mg}} \times \frac{1\text{kg}}{1000\text{ g}}$

$$= 2.5365 \times 10^{-2}\text{ kg}$$

Q. 28. Which one of the following will have largest number of atoms ?
(i) 1 g Au (s) (ii) 1g Na(s) (iii) 1g Li (s)
(iv) 1g of Cl_2 (g)

Ans. No. of atoms can be calculated as :

(*i*) $1\text{g Au} = \frac{1}{197} \times 6.022 \times 10^{23} = \frac{6.022}{197} \times 10^{23}$

(*ii*) $1\text{g Na} = \frac{6.022}{23} \times 10^{23}$

(*iii*) $1\text{g Li} = \frac{6.022 \times 10^{23}}{7}$

(*iv*) $1\text{g } Cl_2 = \frac{2 \times 6.022 \times 10^{23}}{71} = \frac{6.022 \times 10^{23}}{35.5}$

It is clear that 1 g Li contains largest number of atoms.

Q. 29. Calculate the molarity of a solution of ethanol in water in which the mole fraction of ethanol is 0.040.

Ans. Mole fraction of ethanol

$$x(C_2H_5OH) = \frac{n(C_2H_5OH)}{n(C_2H_5OH) + n(H_2O)}$$

To calculate molarity, we need to calculate moles of ethanol in 1 L of solution or nearly 1L of water because the solution is dilute.

$$\text{No. of moles of water in 1 L of water} = \frac{1000}{18} = 55.55\text{ mole}$$

$$\therefore \quad \frac{n(C_2H_5OH)}{n(C_2H_5OH) + 55.55} = 0.040$$

$$n\,(C_2H_5OH) = 0.04\,[n\,(C_2H_5OH)] + 2.222$$

or $\quad 0.96\,n\,(C_2H_5OH) = 2.222$

$$\therefore \quad n = \frac{2.222}{0.96} = 2.31$$

$\therefore$ 2.31 moles of ethanol are present in 1 L of solution and hence, molarity of the solution is **2.31 M**

Q. 30. What will be the mass of one ^{12}C atom in g ?

Ans. 1 mole of ^{12}C atoms = 6.022×10^{23} atoms = 12g

$\therefore$ 6.022×10^{23} atoms of ^{12}C have mass = 12g

$$1\text{ atom of } ^{12}C \text{ will have mass} = \frac{12}{6.022 \times 10^{23}} = 1.9927 \times 10^{-23}\text{ g}$$

Q. 31. How many significant figures should be present in the answer of the following calculations ?

(i) $\frac{0.02856 \times 298.15 \times 0.112}{0.5785}$

(ii) 5×5.364

(iii) 0.0125 + 0.7864 + 0.0215

Ans. *Refer Solved Example 8 (Page 17).*

Q. 32. Use the data given in the following table to calculate the molar mass of naturally occurring argon isotopes :

Isotope	Isotopic molar mass	Abundance
^{36}Ar	35.96755 g mol^{-1}	0.337%
^{38}Ar	37.96272 g mol^{-1}	0.063 %
^{40}Ar	39.9624 g mol^{-1}	99.600 %

Ans. *Refer Solved Example 26 (Page 36).*

Q. 33. Calculate the number of atoms in each of the following :
(i) 52 mol of Ar (ii) 52 u of He (iii) 52 g of He

Ans. *Refer Solved Example 41 (Page 42).*

Q. 34. A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g of carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (mesured at S.T.P.) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula (ii) molar mass of the gas and (iii) molecular formula.

Ans. *Refer Solved Example 66 (Page 55).*

Q. 35. Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction :

$$\mathbf{CaCO_3 + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)}$$

What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 M HCl?

Ans. Let us calculate mass of HCl in 25 mL of 0.75 M HCl

1000 mL of 0.75 M HCl contain HCl = 0.75×36.5 g

$\therefore$ 25 mL of 0.75 M HCl will contain HCl

$$= \frac{0.75 \times 36.5}{1000} \times 25 = 0.684\text{ g}$$

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$
$$100\text{g} \qquad 2 \times 36.5\text{ g}$$

2×36.5 g of HCl react completely with $CaCO_3$ = 100 g

0.684 g of HCl will react completely with $CaCO_3$

$$= \frac{100}{2 \times 36.5} \times 0.684 = \mathbf{0.937\text{ g}}$$

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Q. 36. Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid (HCl) according to the reaction :

$$MnO_2(s) + 4HCl\ (aq) \longrightarrow MnCl_2\ (aq) + 2H_2O(l) + Cl_2(g)$$

How many grams of HCl react with 5.0 g of manganese dioxide ?

Ans. *Refer Solved Example 74 (Page 61).*

NCERT Exemplar Problems

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 123*

Short Answer Questions *Carrying 2 or 3 marks*

Q. 1. What will be the mass of one atom of C-12 in grams ?

Ans. 1 mole of carbon atoms = 12g = 6.022×10^{23} atoms.

6.022×10^{23} atoms of carbon-12 have mass = 12 g

$$\therefore 1 \text{ atom of carbon has mass} = \frac{12}{6.022 \times 10^{23}}$$

$$= 1.99 \times 10^{-23} \text{ g.}$$

Q. 2. How many significant figures should be present in the answer of the following calculations ?

$$\frac{2.5 \times 1.25 \times 3.5}{2.01}$$

Ans. Least precise number in the calculations is 2.5 or 3.5, which has 2 significant figures. Hence the answer should have **two** significant figures.

Q. 3. What is the symbol for SI unit of mole ? How is the mole defined ?

Ans. Symbol for SI unit of mole is mol.

It is defined as the amount of a substance that contains as many particles or entities as there are atoms in 12 g of ^{12}C isotope.

Q. 4. What is the difference between molality and molarity ?

Ans. Molality is the number of moles of solute present in one kilogram of solvent whereas molarity is the number of moles of solute dissolved in one litre of solution.

Molality is independent of temperature whereas molarity depends on temperature.

Q. 5. Calculate the mass percent of calcium, phosphorus and oxygen in calcium phosphate $Ca_3(PO_4)_2$.

Ans. Molecular mass of $Ca_3(PO_4)_2$

$$= 3 \times 40 + 2(31 + 4 \times 16)$$

$$= 310$$

$$\text{Mass of Ca} = 3 \times 40 = 120$$

$$\text{Mass percentage of Ca} = \frac{120}{310} \times 100 = 38.71\%$$

$$\text{Mass of P} = 2 \times 31 = 62$$

Subjective Questions

$$\text{Mass percentage of P} = \frac{62}{310} \times 100 = 20\%$$

$$\text{Mass of O} = 8 \times 16 = 128$$

$$\text{Mass percentage of O} = \frac{128}{310} \times 100 = 41.29\%$$

Q. 6. 45.4L of dinitrogen reacted with 22.7L of dioxygen and 45.4L of nitrous oxide was formed. The reaction is given below :

$$2N_2(g) + O_2(g) \longrightarrow 2N_2O(g)$$

Which law is being obeyed in this experiment ? Write the statement of the law.

Ans. Gases are reacting together to form gaseous products.

Ratio of volumes of gases :

$$N_2 : O_2 : N_2O = 45.4 : 22.7 : 45.4$$

$$= 2 : 1 : 2$$

which is a simple whole number ratio. Hence the experiment proves Gay Lussac's law of gaseous volumes. This law states that gases combine or are produced in a chemical reaction in a simple whole number ratio by volume provided that all gases are at the same temperature and pressure.

Q. 7. If two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in whole number ratio.

(a) Is this statement true ?

(b) If yes, according to which law ?

(c) Give one example related to this law.

Ans. (a) Yes, the given statement is true.

(b) According to the law of multiple proportions.

(c) Hydrogen and oxygen combine to form water (H_2O) and hydrogen peroxide (H_2O_2) as :

$$H_2 + \frac{1}{2}O_2 \longrightarrow \underset{\text{Water}}{H_2O}$$

2 g 16 g 18 g

$$H_2 + O_2 \longrightarrow \underset{\text{Hydrogen peroxide}}{H_2O_2}$$

2 g 32 g 34 g

Masses of oxygen, (*i.e.*, 16 g in H_2O and 32 g in H_2O_2) which combine with fixed mass of hydrogen (2 g) are in the ratio; 16 : 32 or 1 : 2.

This is a simple whole number ratio.

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Q. 8. Calculate the average atomic mass of hydrogen using the following data :

Isotope	% Natural abundance	Molar mass
^1H	99.985	1
^2H	0.015	2

Ans. Average atomic mass $= \dfrac{1 \times 99.985 + 2 \times 0.015}{99.985 + 0.015}$

$= 1.00015$ u.

Q. 9. Hydrogen gas is prepared in the laboratory by reacting dilute HCl with granulated zinc. Following reaction takes place.

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

Calculate the volume of hydrogen gas liberated at STP when 32.65 g of zinc reacts with HCl. 1 mol of a gas occupies 22.7 L volume at STP; Atomic mass of Zn = 65.3 u.

Ans. 1 mol of Zn *i.e.*, 63.5 g of Zn produces 22.7 L of H_2

$\therefore$ 32.65 g of Zn will liberate $H_2 = \dfrac{22.7}{63.5} \times 32.65$

$= \mathbf{11.35\ L}$.

Q. 10. The density of 3 molal solution of NaOH is 1.110 g mL^{-1}. Calculate the molarity of the solution.

Ans. 3 molal solution of NaOH means that 3 mol of NaOH are dissolved in 1000 g of solvent.

Mass of solute = $3 \times 40 = 120$ g

$\therefore$ Mass of solution = Mass of Solvent + Mass of Solute

$= 1000$ g $+ 120$ g $= 1120$ g

Density of solution = 1.110 g mL^{-1}

Volume of solution $= \dfrac{1120}{1.110}$ mL

$= 1009.00$ mL

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Vol. of solution (in mL)}} \times 1000$$

$$= \frac{3}{1009} \times 1000 = \mathbf{2.97\ M}.$$

Q. 11. Volume of a solution changes with change in temperature, then, will the molality of the solution be affected by temperature ? Give reason for your answer.

Ans. No, molality of solution does not change with temperature because it involves masses of solute and solvent which do not change with temperature.

Q. 12. If 4 g of NaOH dissolves in 36 g of H_2O, calculate the mole fraction of each component in the solution. Also, determine the molarity of solution (specific gravity of solution is 1 g mL^{-1}).

Ans. Mass of NaOH = 4 g

Number of moles of NaOH $= \dfrac{4\text{ g}}{40\text{ g}} = 0.1$ mol

Mass of H_2O = 36 g

Number of moles of $H_2O = \dfrac{36\text{ g}}{18\text{ g}} = 2$ mol

Mole fraction of NaOH $= \dfrac{0.1}{2 + 0.1} = \dfrac{0.1}{2.1} = 0.047$

Mole fraction of water $= \dfrac{2}{2 + 0.1} = \dfrac{2}{2.1} = 0.95$

Mass of solution = Mass of water + Mass of NaOH

$= 36$ g $+ 4$ g $= 40$ g

Volume of solution $= 40 \times 1 = 40$ mL

(Since specific gravity of solution is 1 g mL^{-1})

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution (in mL)}} \times 1000$$

$$= \frac{0.1}{40} \times 1000 = 2.5\ \text{M}.$$

Q. 13. The reactant which is entirely consumed in reaction is known as limiting reagent. In the reaction $2A + 4B \rightarrow 3C + 4D$, when 5 moles of A react with 6 moles of B, then

(*i*) which is the limiting reagent ?

(*ii*) calculate the amount of C formed ?

Ans. *Refer Conceptual Questions* 3, *Q.9 (Page 77).*

Long Answer Questions *carrying 5 marks*

Q. 14. A vessel contains 1.6 g of dioxygen at STP (273.15K, 1 atm pressure). The gas is now transferred to another vessel at constant temperature, where pressure becomes half of the original pressure. Calculate

(*i*) volume of the new vessel.

(*ii*) number of molecules of dioxygen.

Ans. (*i*) Moles of oxygen $= \dfrac{1.6}{32} = 0.05$ mol

1 mol of O_2 at STP has volume = 22.4 L

0.05 mol of O_2 at STP has volume $= 22.4 \times 0.05$

$= 1.12$ L

$V_1 = 1.12$ L $\quad p_1 = 1$ atm

$V_2 = ?$ $\quad p_2 = \dfrac{1}{2} = 0.5$ atm.

According to Boyle's law (unit 4)

$p_1V_1 = p_2V_2$

or $V_2 = \dfrac{p_1V_1}{p_2} = \dfrac{1\text{ atm} \times 1.12\text{ L}}{0.5\text{ atm}} = 2.24$ L

(*ii*) No. of molecules in 1.6 g or 0.05 mol

$= 6.022 \times 10^{23} \times 0.05 = \mathbf{3.011 \times 10^{22}}$.

Q. 15. Calcium carbonate reacts wth aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction given below :

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

What mass of $CaCl_2$ will be formed when 250 mL of 0.76 M HCl reacts with 1000 g of $CaCO_3$? Name the limiting reagent. Calculate the

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number of moles of $CaCl_2$ formed in the reaction.

Ans. *Refer Solved Example 124 (Page 75).*

Q. 16. Define the law of multiple proportions. Explain it with two examples. How does this law point to the existence of atoms ?

Ans. *Refer Text (Page 24).*

Q. 17. A box contains some identical red coloured balls, labelled as A, each weighing 2 grams. Another box contains identical blue coloured balls, labelled as B, each weighing 5 grams. Consider the combinations AB, AB_2, A_2B and A_2B_3 and show that law of multiple proportions is applicable.

Ans.

Combination of A and B	AB	AB_2	A_2B	A_2B_3
Mass of A (in g)	2	2	4	4
Mass of B (in g)	5	10	5	15

Masses of B which combine with fixed mass of A (say 4 g) are :

10 g , 20 g , 5 g , 15 g

Ratio 2 : 4 : 1 : 3

This is a simple whole number ratio. Hence the law of multiple proportions is applicable.

QUICK MEMORY TEST

A. Say True or False

1. Properties of a compound are average of the properties of its constituent atoms.
2. There is no difference in writing mass of an object as 7.00 g or 7.0 g.
3. The number of ozone molecules present in 1 mole of ozone are 6.022×10^{23}.
4. There is no difference between mass and weight of a substance.
5. Balancing of chemical equations is in accordance with the law of conservation of mass.
6. Homogeneous mixtures have sharp melting and boiling points.
7. The figure 0.02450 has 4 significant figures.
8. There is no difference between 0.005 or 5.00×10^{-3} g.
9. The empirical and molecular formula of sucrose is same.
10. 0.5 mole of S_8 and 0.5 mol of P_4 have same number of polyatomic molecules.
11. Molarity of a solution changes with temperature but molality does not.
12. The empirical formula of glucose is CH_2O.
13. 1 gram atom of C and 1 gram atom of sulphur have same mass.
14. When 3.0 g of H_2 react with 29.0g of O_2 to form water, O_2 is the limiting reactant.
15. Nitrogen and oxygen combine to form N_2O, NO and NO_2. This is in accordance with law of reciprocal proportions.

B. Complete the missing links

1. AZT is used for the victims of .....
2. The prefix pico stands for .....
3. Pascal are the units for the physical quantity .....
4. The number of significant figures in 0.00030 is .....
5. Decimal equivalent of 2/3 is ..... upto three significant figures.
6. The empirical formula of hydrogen peroxide is .....
7. The law which does not follow from Dalton's atomic theory is .....
8. The mass of a molecule of carbon-14 dioxide ($^{14}CO_2$) is ..... g.
9. An atom of sulphur is ..... times heavier than an atom of carbon.
10. The ratio of atoms of hydrogen in 1 mole of methane and 1 mole of sucrose ($C_{12}H_{22}O_{11}$) is ..... .
11. ..... mol of N_2 are needed to produce 3.8 mol of NH_3 by reaction with hydrogen.
12. If mole fraction of sodium chloride in sodium chloride aqueous solution is 0.35, then mole fraction of water in the solution is ..... .
13. The molarity of 0.5 N H_2SO_4 solution is ..... M.
14. Amount of glucose ($C_6H_{12}O_6$) required to prepare 100 mL of 0.1 M solution is .....
15. The empirical formula of benzene is .....

C. Choose the correct alternative

1. When 50g of N_2 and 10g of H_2 are mixed to produce NH_3; the limiting reagent is *N_2/H_2*.
2. Out of molarity and mole fraction; *molarity/mole fraction* is independent of temperature.
3. 1 gram mole of CO_2 has *less/more* mass than 1 gram mole of CO.
4. Empirical and molecular formula are *same/different* of acetylene.

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5. Law of multiple proportion was stated by *Dalton/Proust*.
6. 1 femtometer is equal to $10^{-15}/10^{-18}$ m.
7. The units kg $m^{-1}s^{-2}$ are of *force/pressure*.
8. 0.0030 has *two/four* significant figures.
9. The sum 4.524 + 2.3 + 6.24 is equal to *13.1/13.06*.
10. Mass of 1*cc* of H_2 at STP is $9.0 \times 10^{-5}g/1g$.

Answers QUICK MEMORY TEST

A. Say True or False

1. **False :** Properties of a compound are entirely different from those of the constituent atoms.
2. **False :** because 7.00 g is more precise than 7.0 g.
3. True
4. **False :** Mass of a substance is a constant quantity but its weight varies from place to place.
5. True
6. **False :** Homogeneous as well as heterogeneous mixtures do not have sharp melting and boiling points.
7. True
8. **False :** 0.006 g contains one significant figure while 5.00×10^{-3} contains 3 significant figures.
9. True
10. True
11. True
12. True
13. False
14. False
15. False.

B. Complete the missing links

1. AIDS
2. 10^{-12}
3. Pressure
4. two
5. 0.667
6. HO
7. Gay-Lussac law of gaseous volumes
8. 7.64×10^{-23}
9. 8/3
10. 2 : 11
11. 1.9
12. 0.65
13. 0.25
14. 1.8 g
15. CH

C. Choose the correct alternative

1. H_2
2. mole fraction
3. more
4. different
5. Dalton
6. 10^{-15}
7. pressure
8. two
9. 13.1
10. 9.0×10^{-5} g.

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. In the combustion of methane in air, what is the limiting reactant and why ?

Ans. Methane is the limiting reactant because the other reactant is oxygen of the air which is always present in excess. Thus, the amounts of carbon dioxide and water formed will depend upon the amount of CH_4 burnt.

Q.2. What is kg-mole ? How many electrons are present in 1 kg mole of methane (CH_4)?

Ans. One kg-mole is the molecular mass of the substance expressed in kilograms. It is also called kilomole (k mol). One k mol contains 6.022×10^{26} particles. Thus,

1kg-mole of CH_4 contains 6.022×10^{26} molecules.

Since one molecule of methane contains 10 electrons and therefore, 1 kg mole of CH_4 contains $10 \times 6.022 \times 10^{26} = 6.022 \times 10^{27}$ electrons.

Q.3. Which aqueous solution has higher concentration : 1 molar or 1 molal solution of the same solute. Give reason.

Ans. 1 molar aqueous solution has higher concentration than 1 molal solution.

A molar solution contains one mole of solute in one litre of solution while a one molal solution contains one mole of solute in 1000 g of solvent.

If density of water is 1, then one mole of solute is present in 1000 mL of water in 1 molal solution while one mole of solute is present in less than 1000 mL of water in 1 molar solution (1000 mL solution = amount of solute + amount of solvent). Thus, 1 molar solution is more concentrated.

Q.4. Will the molarity of a solution at 50°C be same, less or more than molarity at 25°C?

Ans. Molarity at 50°C of a solution will be less than that at 25°C because molarity decreases with increase in temperature. This is because volume of the solution increases with increase in temperature but number of moles of solution remain the same.

Q.5. Is the law of constant composition true for all types of compounds ? Explain why or why not.

Ans. No, law of constant composition is not true for all types of compounds. It is true for only those compounds which are obtained from one isotope. For example, carbon exists in two common isotopes : ^{12}C and ^{14}C. When it forms $^{12}CO_2$, the ratio of masses is 12 : 32 or 3 : 8. However, when it is formed from ^{14}C i.e., $^{14}CO_2$, the ratio will be 14 : 32 *i.e.*, 7 : 16, which is not same as in the first case.

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Q.6. Why is molality preferred over molarity in expressing the concentration of a solution ?

Ans. Molality is the number of moles of a solute present in 1000 g of the solvent while molarity is the number of moles of solute present in 1000 mL of the solution. Thus, molality involves only masses which donot change with temperature whereas molarity involves volume which changes with temperature and hence molality is preferred over molarity.

Q.7. What is the difference in expressing a weight of a solid as 36.5×10^3 g and 36.50×10^3 g ?

Ans. 36.5×10^3 g has three significant figures while 36.50×10^3 has four significant figures. Hence 36.50 represents greater accuracy than 36.5.

Q.8. How many significant figures are there in 'π' ?

Ans. Infinite number.

Q.9. In calculations involving more than one arithmetic operation, rounding off to the proper number of significant figures may be done once at the end if all the operations are multiplication and/or division or if they are all additions and/or subtractions but not if they are combinations of additions or subtractions with multiplications or divisions. Explain.

Ans. There are different rules for the number of significant digits in the answer to an addition or subtraction and to a multiplication or division. Therefore, they must be applied separately when a mixed calculation is performed.

Q.10. Calculate the molarity of water if its density is 1000 kg/m^3.

Ans. Molarity of water means the number of moles of water in 1 litre of water.

1 L of water = 1000 cm^3 = 1000 g

($\because$ 1000 kg/m^3 = 1g/cm^3)

$$1000 \text{ g of water} = \frac{1000}{18}$$

$$= 55.56 \text{ moles}$$

$\therefore$ Molarity = **55.56 M.**

Q.11. Sulphuric acid is generally available in market as 18.0 M solution. How would you prepare 250 mL of 0.50 M aqueous H_2SO_4?

Ans. Applying molarity equation,

$$M_1V_1 = M_2V_2$$

Volume of 18 M (V_2) H_2SO_4 required to prepare 250 mL (V_1) of concentration 0.50 M (M_1).

$$0.50 \times 250 = 18 \times V_2$$

$$\therefore \quad V_2 = \frac{0.50 \times 250}{18} = 6.94 \text{ mL}$$

Volume of 18 M H_2SO_4 required = 6.94 mL

Volume of water required = 250 – 6.94 = **243.06 mL**

Q.12. A compound (molecular mass = 246) has the following data :

Element	% Composition	Relative no. of atoms
A	9.76	0.406
B	13.01	0.406
C	26.01	1.625
D	51.22	2.846

From the data find out

(*i*) atomic masses of the elements A, B, C and D,

(*ii*) simple ratio,

(*iii*) molecular formula of the compound.

Ans. Step I. *To calculate the atomic masses :*

The relative number of atoms

$$= \frac{\text{Percentage of element}}{\text{Atomic mass}}$$

$$\text{Atomic mass} = \frac{\text{Percentage of element}}{\text{Relative number of atoms}}$$

$\therefore$ Atomic mass of A $= \frac{9.76}{0.406} = 24,$

Atomic mass of B $= \frac{13.01}{0.406} = 32$

$\therefore$ Atomic mass of C $= \frac{26.01}{1.625} = 16,$

Atomic mass of D $= \frac{51.22}{2.846} = 18$

Step II. *To calculate the simple ratio of atoms.*

Element	Relative no. of atoms	Simple atomic ratio
A	0.406	$\frac{0.406}{0.406} = 1$
B	0.406	$\frac{0.406}{0.406} = 1$
C	1.625	$\frac{1.625}{0.406} = 4$
D	2.846	$\frac{2.846}{0.406} = 7$

Thus, the atomic ratio of A : B : C : D is 1: 1 : 4 : 7.

Hence, the empirical formula = **ABC_4D_7.**

Step III. *Calculation of molecular formula*

Empirical formula mass = 24 + 32 + 4 × 16 + 7 × 18

= 246

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{246}{246} = 1$$

Molecular formula of compound = $(ABC_4D_7)_1$

= **ABC_4D_7**

Q.13. A compound on analysis gave the following percentage composition : Sodium = 18.59%, Sulphur = 25.80%, Hydrogen = 4.03% and Oxygen = 51.58%. Calculate the molecular formula of crystalline salt on the assumption that all the hydrogen atoms in the compound are present in combination with oxygen as water of crystallisation. The molecular weight of the compound is 248 a.m.u.

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Solution.

Step I. *Calculation of empirical formula*

Element	Percentage of element	At. mass	Moles of atoms	Mole ratio
Na	18.59	23	$\frac{18.59}{23} = 0.80$	$\frac{0.80}{0.80} = 1$
S	25.80	32	$\frac{25.80}{32} = 0.80$	$\frac{0.80}{0.80} = 1$
H	4.03	1	$\frac{4.03}{1} = 4.03$	$\frac{4.03}{0.80} = 5$
O	51.58	16	$\frac{51.58}{16} = 3.22$	$\frac{3.22}{0.80} = 4$

Thus, the simple ratio of Na : S : H : O is 1 : 1 : 5 : 4. Therefore, the empirical formula of the compound is $NaSH_5O_4$.

Step II. *Calculation of molecular formula*

Empirical formula mass = 23 + 32 + 5 × 1 + 4 × 16 = 124

Molecular mass = 248

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{248}{124} = 2$$

$\therefore$ Molecular formula = $(NaSH_5O_4)_2$ = $Na_2S_2H_{10}O_8$

Since all the 10 hydrogen atoms are present as water molecules (H_2O), the total number of water molecules is $5H_2O$.

Molecular formula = $\mathbf{Na_2S_2O_3 . 5H_2O}$

Q.14. The vapour density of a mixture of NO_2 and N_2O_4 is 38.3 at 26.7°C. Calculate the number of moles of NO_2 in 100 g of the mixture.

Ans. V.D. of mixture of NO_2 and N_2O_4 = 38.3

Mol. wt. of mixture of NO_2 and N_2O_4 = 38.3 × 2 = 76.6 (Mol. wt. = 2 × V.D.)

Let NO_2 present in 100 g of mixture = x

N_2O_4 present in 100 g of mixture = $100 - x$

Mol. wt. of NO_2 = 46, Mol. wt. of N_2O_4 = 92

Now, $$\frac{x}{46} + \frac{100 - x}{92} = \frac{100}{76.6}$$

Solving for x, we get x = 20.1 g

$\therefore$ Moles of NO_2 in the mixture = $\frac{20.1}{46}$ = **0.437**

Q.15. A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate is heated below 600°C until the weight of the residue was constant. If the loss in weight is 28.0%, calculate the amount of lead nitrate and sodium nitrate in the mixture.

Ans. Let the amount of $NaNO_3$ in the mixture = x g

Amount of $Pb(NO_3)_2$ in the mixture = $(5 - x)$ g

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2\uparrow$$
$$2(23 + 14 + 3 \times 16) \quad 2 \times 16$$
$$= 170 \text{ g} \quad = 32$$

$$2Pb(NO_3)_2 \longrightarrow 2PbO + O_2\uparrow + 4NO_2\uparrow$$
$$2(207 + 28 + 96) \quad 2 \times 16 \quad 4 \times (14 + 32)$$
$$= 662 \text{ g} \quad = 32 \quad = 184 \text{ g}$$

170 g of $NaNO_3$ give O_2 = 32 g

x g of $NaNO_3$ give $O_2 = \frac{32}{170} \times x$ g

Similarly,

662 g of $Pb(NO_3)_2$ give O_2 and NO = 216 g

$(5 - x)$ g of $Pb(NO_3)_2$ give gases $= \frac{216}{662} \times (5 - x)$ g

Total loss on heating $= \frac{32x}{170} + \frac{216}{662}(5 - x)$

Actual loss on heating = 28% of 5 g $= \frac{28 \times 5}{100} = 1.4$ g

$\therefore$ $\frac{32x}{170} + \frac{216}{662}(5 - x) = 1.4$

Solving for x, we get x = 1.676 g

$\therefore$ Wt. of $NaNO_3$ = **1.676 g**

Wt. of $Pb(NO_3)_2$ = 5 – 1.676 = **3.324 g.**

Q.16. A sample of hard water contains 20 mg of Ca^{2+} ions per litre. How many milliequivalents of Na_2CO_3 would be required to soften 1 litre of sample ?

Ans. $$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$$
$$40 \text{ g} \quad 106 \text{ g}$$

40 g of Ca^{2+} react with Na_2CO_3 = 106 g

20×10^{-3} g of Ca^{2+} react with $Na_2CO_3 = \frac{106}{40} \times 20 \times 10^{-3}$ = 5.3×10^{-2} g

Eq. wt. of $Na_2CO_3 = \frac{\text{Mol. wt.}}{2} = \frac{106}{2} = 53$

Equivalents of $Na_2CO_3 = \frac{5.3 \times 10^{-2}}{53} = 1 \times 10^{-3}$ equiv.

Milliequivalents of $Na_2CO_3 = \frac{1 \times 10^{-3}}{10^{-3}}$ = **1 milliequivalent.**

Q.17. Igniting MnO_2 converts it quantitatively to Mn_3O_4. A sample of pyrolusite is of the following composition :

MnO_2 = 80%, SiO_2 and other inert contents = 15%, rest being water.

The sample is ignited in air to constant weight. What is the percentage of Mn in the ignited sample ? (At. wt. of Mn = 55).

Ans. $$3MnO_2 \longrightarrow Mn_3O_4 + O_2$$
$$3(55 + 2 \times 16) \quad 3 \times 55 + 4 \times 16$$
$$= 261 \text{ g} \quad = 229 \text{ g}$$

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Let the amount of pyrolusite ignited = 100 g

Wt. of MnO_2 = 80 g

Wt. of SiO_2 and other inert contents = 15 g

Wt. of water = 100 – (80 + 15) = 5 g

Now, 261 g of MnO_2 gives Mn_3O_4 = 229 g

$$80 \text{ g of } MnO_2 \text{ give } Mn_3O_4 = \frac{229}{261} \times 80$$

$$= 70.19 \text{ g.}$$

During ignition, water present in pyrolusite is removed while SiO_2 and other inert contents remain as such.

Total wt. of residue = 70.19 + 15 = 85.19 g

$$\therefore \text{Percentage of } Mn_3O_4 \text{ in the residue} = \frac{70.19}{85.19} \times 100$$

$$= 82.39\%$$

Now 3 Mn = Mn_3O_4

3×55 $3 \times 55 + 4 \times 16$

$= 165$ $= 229$

$\therefore$ 229 g of Mn_3O_4 contain Mn = 165

$$82.39 \text{ g of } Mn_3O_4 \text{ contain Mn} = \frac{165}{229} \times 82.39$$

$$= 59.36 \text{ g}$$

$\therefore$ Percentage of Mn in ignited sample = **59.36%**

Q.18. The density of gold is 19.3 g cm^{-3}. Calculate the diameter of a solid gold sphere having a mass of 422 g.

Ans. Volume of gold sphere = $\frac{\text{Mass}}{\text{Density}}$

$$= \frac{422 \text{ g}}{19.3 \text{ g cm}^{-3}}$$

$$= 21.865 \text{ cm}^3$$

$$\text{Volume of sphere} = \frac{4}{3}\pi r^3$$

$$\text{or radius, } r = \left(\text{Volume} \times \frac{3}{4\pi}\right)^{1/3}$$

$$= \left(\frac{21.865 \times 3 \times 7}{4 \times 22}\right)^{1/3}$$

$$= (5.218)^{1/3} = 1.73 \text{ cm}$$

$$\therefore \text{Diameter} = 2 \times r$$

$$= 1.73 \times 2 = \mathbf{3.46 \text{ cm}}$$

Q.19. Lithium oxide is used to remove water from air according to the reaction :

$$\mathbf{Li_2O(s) + H_2O(g) \longrightarrow 2LiOH(s)}$$

If 72 kg of water is to be removed and 35 kg of Li_2O is available

(*i*) which reactant is limiting ?

(*ii*) how many kg of excess reactant is left ?

Ans. Moles of water = $\frac{72 \times 10^3}{18}$

$$= 4 \times 10^3 \text{ mol}$$

Moles of Li_2O = $\frac{35 \times 10^3}{30}$

$$= 1.167 \times 10^3 \text{ mol}$$

(*i*) Li_2O is limiting reagent because 1 mole of Li_2O reacts with 1 mole of water.

(*ii*) Moles of water which will react = 1.167×10^3 mol

Moles of water left unreacted

$$= 4 \times 10^3 - 1.167 \times 10^3$$

$$= 2.833 \times 10^3$$

Mass of water left = $2.833 \times 10^3 \times 18$

$$= \mathbf{50.99 \text{ kg}}$$

Q.20. P_4O_6 and P_4O_{10} are formed by burning P_4 with O_2 as :

$$\mathbf{P_4 + 3O_2 \longrightarrow P_4O_6}$$

$$\mathbf{P_4 + 5O_2 \longrightarrow P_4O_{10}}$$

What are the masses of P_4O_6 and P_4O_{10} that will be produced by the combustion of 2.0 g of P_4 in 2.0 g of oxygen leaving no P_4 and O_2 ?

Ans. P_4O_6 and P_4O_{10} are formed as :

$$P_4 + 3O_2 \longrightarrow P_4O_6$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

Let x be the mass of P_4 that is converted into P_4O_6 so that

Mass of P_4 which is converted to $P_4O_{10} = 2 - x$

Mass of oxygen required for forming P_4O_6

$$= \frac{x}{4 \times 31} \times 96$$

Mass of oxygen required for forming P_4O_{10}

$$= \frac{2 - x}{4 \times 31} \times 160$$

Total oxygen required,

$$\left(\frac{x}{4 \times 31} \times 96\right) + \left(\frac{2 - x}{4 \times 31} \times 160\right) = 2.0$$

$$\text{or } \frac{96x}{124} + \frac{320}{124} - \frac{160x}{124} = 2.0$$

$$\text{or } -\frac{64x}{124} = 2.0 - \frac{320}{124}$$

$$\text{or } -\frac{64x}{124} = -\frac{72}{124}$$

$$x = \frac{72}{64} = 1.125 \text{ g}$$

Mass of P_4O_6 formed

$$= \frac{\text{Mass of } P_4}{\text{Molar mass of } P_4} \times \text{Molar mass of } P_4O_6$$

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$$= \frac{1.125}{124} \times 220 = 1.996\,g$$

Mass of P_4O_{10} formed

$$= \frac{\text{Mass of } P_4}{\text{Molar mass of } P_4} \times \text{Molar mass of } P_4O_{10}$$

$$= \frac{0.875}{124} \times 284 = 2.004\,g$$

Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. Define Avogadro's law.
2. What is meant by a.m.u. ?
3. Define significant figure.
4. What is a mole ?
5. Define precision.
6. State the law of definite proportions.
7. Define atomic mass of an element.
8. Does a balanced chemical equation obey the law of conservation of mass ?
9. Define molarity of a solution.
10. Express decimal equivalent of 2/7 to three significant figures.
11. Is the molar volume of NH_3 different from that of CO_2 ?
12. Name a monoatomic gas ? What is its valency ?
13. Define limiting reagent.
14. Write 0.000623 cm in a scientific notation.
15. Define law of multiple proportions.
16. What is gram molecular mass ? Give one example.
17. Give one example each of a molecule in which empirical formula and molecular formula are
    (*i*) same and (*ii*) different.
18. Define mole in terms of number.
19. Balance the equation :
    $CaF_2 + H_2SO_4 + H_3BO_3 \longrightarrow CaSO_4 + BF_3 + H_2O$
20. How many atoms of carbon are present in 0.1 mole of $C_{12}H_{22}O_{11}$?
21. How many hydrogen atoms are present in 60 a.m.u. of ethane ?
22. What is meant by one gram of atom of iron ?
23. What is the S.I. unit of density ?
24. Name the law which deals with the ratios of the volumes of the gaseous reactants and products.
25. Which isotope of C is used for expressing relative atomic masses of elements ?
26. An atom of an element is 13 times heavier than the mass of a carbon atom. What is its mass in a.m.u. ?
27. What is the standard for the molecular weights of molecules ?
28. What is the ratio of molar volumes of SO_2 and SO_3 ?
29. State law of reciprocal proportions.
30. What volume will 250 g of mercury occupy ? (Density of mercury = 13.6 g cm^{-3}).

Short Answer Questions *Carrying 2 or 3 marks*

1. What do you understand by the terms element, compound and mixture ? Give two examples in each case.
2. Explain the term mole. What does one mole of ammonia represent ?
3. Give the SI units for (*i*) volume (*ii*) speed and (*iii*) force.
4. What do you understand by the terms (*i*) empirical formula and (*ii*) molecular formula ? How are they related to each other ? Illustrate with an example.
5. Define molarity. What does 1 M solution of sodium carbonate mean ?
6. Classify the following into elements, compounds or mixtures :
   (*i*) Water (*ii*) milk (*iii*) tea (*iv*) iron (*v*) sugar (*vi*) smoke (*vii*) sulphur (*viii*) 22 carat gold (*ix*) iodised table salt (*x*) gasoline.
7. What are homogeneous and heterogeneous mixtures ? Which of the following are homogeneous ?
   (*a*) tap water (*b*) wood (*c*) soil (*d*) smoke (*e*) cloud.
8. When two substances A and B are mixed together in a pestel and mortar, a large amount of heat is evolved and a new substance C is formed. C has the properties different from A and B. Is C an element, compound or a mixture?
9. State the following :
   (*i*) atomic mass (*ii*) gram atomic mass (*iii*) gram molar volume.
10. How would you recover
    (*i*) iodine from a mixture of iodine and salt?
    (*ii*) sulphur from a mixture of carbon and sulphur ?
11. State Avogadro's hypothesis. In what way, has it given support to Dalton atomic theory ?
12. How can you deduce the atomicity of hydrogen with the help of Avogadro's hypothesis ?
13. State the following laws of chemical combination and give one example in each case
    (*i*) Law of constant composition.
    (*ii*) Law of multiple proportions.

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14. What do you understand by a balanced chemical equation ? What quantitative information does a balanced chemical equation convey ?
15. Explain (*i*) molarity (*ii*) limiting reagent.
16. Write the balanced chemical equations for the following reactions :
    (*i*) Manganese dioxide and concentrated hydrochloric acid.
    (*ii*) Sodium thiosulphate and iodine.
    (*iii*) Copper and dilute nitric acid.
    (*iv*) Sulphur dioxide and hydrogen sulphide.
17. Write the empirical formulae of the compounds having the following molecular formulae :
    (*i*) C_6H_6 (*ii*) C_6H_{12} (*iii*) H_2O_2 (*iv*) H_2O
    (*v*) Na_2CO_3 (*vi*) B_2H_6 (*vii*) N_2O_4.
18. Balance the following equations :
    (*i*) $H_3PO_3 \longrightarrow H_3PO_4 + PH_3$
    (*ii*) $Ca + H_2O \longrightarrow Ca(OH)_2 + H_2$
    (*iii*) $Fe_2(SO_4)_3 + NH_3 + H_2O \longrightarrow Fe(OH)_3 + (NH_4)_2SO_4$
19. What do you understand by the term formula mass ? How does it differ from molecular mass ?
20. Which of the following has (*i*) maximum (*ii*) minimum mass ?
    (*a*) 1 gram atom of C
    (*b*) 1 a.m.u. of an atom
    (*c*) 1 gram mole of sulphur dioxide
    (*d*) 6.02×10^{20} atoms of nitrogen.

Long Answer Questions *carrying 5 marks*

1. State the law of conservation of mass. How is it verified experimentally ?
2. What are laws of chemical combinations ? Discuss any three laws in detail.
3. Why is it necessary to balance a chemical equation ? Outline briefly the various steps for balancing a chemical equation by hit and trial method.
4. Write short notes on
   (*i*) Limiting reagent (*ii*) Avogadro hypothesis
   (*iii*) Dalton's atomic theory.
5. How is mole related to
   (*i*) mass (*ii*) volume and (*iii*) number of molecules of a substance ?
6. Complete the following :

   $CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$

(*a*)	2 moles	.....	.....	
(*b*)	..... g	.....g	.....g	.....2g.
(*c*)	..... H atoms	..... H atoms	6×10^{23} H atoms	..... H atoms
(*d*)	6×10^{20} ..... total	.....total atoms	.....total atoms	.....total atoms

7. What are the main postulates of Dalton's atomic theory ? What were its limitations ? How has the theory been modified ?
8. Define Avogadro number and mole. What is their importance ?
9. What are the essentials of a chemical equation ? What is the information conveyed by a chemical equation ?
10. Explain the following :
    (*a*) Gay Lussac law
    (*b*) Law of definite composition
    (*c*) Empirical and molecular formula
    (*d*) Relation between mole and volume of gases
    (*e*) Limiting reagent.

Numerical Problems *carrying 5 marks*

1. State the number of significant figures in each of the following :
   (*a*) 0.0037 (*b*) 0.00601
   (*c*) 1.0001 (*d*) 0.00236
   (*e*) 1.06×10^{-3}
2. Express the following numbers to three significant figures :
   (*a*) 6.0263 (*b*) 2.3652
   (*c*) sixty thousand (*d*) 2.861×10^5
3. Express the result of the following calculations to appropriate number of significant figures :
   (*a*) $\dfrac{7.5 \times 206.8}{0.0512 \times 1002}$
   (*b*) 4.20 + 1.6523 + 0.015
   (*c*) (1.0042 – 0.0034) (1.23)
   (*d*) $\dfrac{8.5 \times 208.9}{0.054 \times 9291.6}$
4. Carbon and oxygen combine to form two oxides having the composition : 1st oxide C = 42.9% and II oxide C = 27.3%. Show that the data is in agreement with the law of multiple proportions.
5. Calculate the amount in grams of :
   (*a*) 2.5 gram atoms of nitrogen
   (*b*) 3.6 gram mole of carbon dioxide
6. Calculate (*i*) number of molecules present in 2.24 dm^3 of carbon dioxide at N.T.P.
   (*ii*) mass of an atom of oxygen
   (*iii*) number of oxygen atoms in 2 mol of ozone
   (*iv*) volume occupied by 4.4 g of SO_2 at N.T.P.
7. One atom of nickel weighs 9.75×10^{-23} g. Calculate the atomic mass of nickel.
8. How many molecules are present in 1 kg of hydrogen ?
9. Calculate the total charge of a mole of electrons if the electrical charge on a single electron is 1.60×10^{-19} C.
10. The volume of a drop of rain was found to be 0.448 ml at N.T.P. How many molecules of water and number of atoms of hydrogen are present in this drop ?
11. Calculate the number of molecules of oxygen in 150 ml of it at 20°C and 750 mm pressure.
12. Assuming the atomic mass of a metal M to be 56, calculate the empirical formula of its oxide containing 70.0% M.

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13. How many moles of hydrogen, phosphorus and oxygen are there in 0.4 moles of phosphoric acid (H_3PO_4) ?

14. A solution has been prepared by dissolving 5.6 g of KOH in 250 mL of it. Calculate the molarity of the solution.

15. A chemist wishes to prepare 6.022×10^{24} molecules of SO_2 according to the reaction :

$$S + O_2 \longrightarrow SO_2$$

How many gram atoms of S and how many grams of O does he need ?

16. A sample of iron has a mass of 1.68 g. Calculate (*a*) the number of moles of iron present, (*b*) the number of atoms of iron in the sample.

17. 2.5 g of an impure sample of sodium bicarbonate when heated strongly gave 300 ml of carbon dioxide measured at 27°C and 760 mm pressure. Calculate the percentage purity of the sample.

18. Which is cheaper ?

40% HCl at the rate of ₹ 6 per kg or 80% H_2SO_4 at the rate of ₹ 3.5 per kg required to neutralise 7 kg of KOH.

19. The compound adrenaline is released in the human body in times of stress. It was found by experiment to have the composition 56.8 % C, 6.50 % H, 28.4% O and 8.28% N. What is the empirical formula of adrenaline?

20. What volume of concentrated aqueous sulphuric acid which is 98.0% H_2SO_4 by mass and has a density of 1.84 g mL^{-1} is required to prepare 10.0 L of 0.200 M H_2SO_4 solution ?

Hints & Answers *for* Revision Exercises

Very Short Answer Questions

10. 0.286

11. Both have same molar volume

12. He, valency = 0

14. 6.23×10^{-4}

17. (*i*) CO_2 (*ii*) C_6H_6

19. $3CaF_2 + 3H_2SO_4 + 2H_3BO_3 \longrightarrow 3CaSO_4 + 2BF_3 + 6H_2O$

20. 7.224×10^{23}

21. 12

22. One gram atom of iron means atomic mass of iron expressed in grams. It is equal to 56 g.

23. kg m^{-3}

24. Gay Lussac law

25. ^{12}C

26. 13 × 12 = 156 a.m.u.

27. C^{12}

28. 1 : 1

29. $\frac{250}{13.6}$ = 18.4 g cm^{-3}

Short Answer Questions

3. (*i*) m^3 (*ii*) m s^{-1} (*iii*) kg m s^{-2} or N

6. Compounds : (*i*), (*v*) ;
Mixtures : (*ii*), (*iii*), (*vi*), (*viii*), (*x*);
Elements (*iv*), (*vii*).

7. Tap water and clouds are homogeneous.

18. (*i*) $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$
(*ii*) $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$
(*iii*) $Fe_2(SO_4)_3 + 3NH_3 + 3H_2O \longrightarrow 2Fe(OH)_3 + 3(NH_4)_2SO_4$

20. (*i*) (*c*) (*ii*) (*b*).

Long Answer Questions

6. (*a*) 4, 2, 4 moles (*b*) 21, 18, 37 g
(*c*) 6×10^3, 12×10^3, 12×10^3 H atoms
(*d*) 12×10^{20}, 10×10^{20}, 8×10^{20}

Numerical Problems

1. (*a*) 2, (*b*) 3, (*c*) 5, (*d*) 3, (*e*) 3

2. (*a*) 6.03, (*b*) 2.36, (*c*) 6.00×10^4, (*d*) 2.86

3. (*a*) $\frac{7.5 \times 206.8}{0.0512 \times 1002}$ = 30.232 = **30.**
7.5 contains only two significant figures and therefore, the result is reported to 2 significant figures.

(*b*) 4.20
1.6523
0.015
5.8673= **5.87** [upto two decimal places (as in 4.20]

(*c*) (1.0042 – 0.0034) (1.23)
(1.0008) (1.23) = 1.230984 = **1.23** [upto 3 significant figures]

(*d*) $\frac{8.5 \times 208.9}{0.054 \times 9291.6}$ = 3.5389 = **3.5** (upto 2 significant figures as in 8.5)

4. *Ist oxide*

Mass of carbon = 42.9 g
Mass of oxygen = 100 – 42.9 = 57.1 g

Second oxide

Mass of carbon = 27.3 g
Mass of oxygen = 100 – 27.3 = 72.7 g

Let us fix the mass of carbon as 1g

In first oxide,

Mass of oxygen combining with 42.9 g of carbon = 57.1 g

Mass of oxygen combining with 1g of carbon = $\frac{57.1}{42.9}$ = 1.33 g

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In second oxide,

Mass of oxygen combining with 27.3 g of carbon = 72.7 g

Mass of oxygen combining with 1g of carbon $= \frac{72.7}{27.3} = 2.66$ g

Ratio of oxygen combining with 1g of carbon

1.33 : 2.66

1 : 2

This is a simple whole number ratio and therefore, it is in agreement with **law of multiple proportions.**

5. (*a*) 1 gram atom of nitrogen = 14 g

2.5 gram atoms of nitrogen = 14 × 2.5 = **35 g.**

(*b*)1 gram mole of carbon dioxide = 44 g

3.6 gram mole of carbon dioxide = 44 × 3.6 = **158.4 g.**

6. (*i*) 22.4 dm^3 of CO_2 at N.T.P. has molecules = 6.02×10^{23}

2.24 dm^3 of CO_2 at N.T.P. has molecules $= \frac{6.02\times10^{23}}{22.4}\times 2.24$

= **6.02×10^{22}.**

(*ii*) Mass of 6.02×10^{23} atoms of oxygen = 16 g

Mass of 1 atom of oxygen $= \frac{16}{6.02\times10^{23}} =$ **2.66×10^{-23} g.**

(*iii*) No. of ozone molecules in 2 mol = $6.02 \times 10^{23} \times 2$

One ozone molecule = 3 atoms of oxygen

No. of oxygen atoms in 2 mol of ozone = $6.02 \times 10^{23} \times 2 \times 3$

= **3.61×10^{24}.**

(*iv*) Molecular mass of SO_2 = 64

64 g of SO_2 at N.T.P. occupy volume = 22.4 L

4.4 g of SO_2 at N.T.P. occupy volume $= \frac{22.4}{64} \times 4.4$

= **1.54 L.**

7. Atomic mass is the mass of 6.022×10^{23} atoms

Mass of 6.022×10^{23} atoms of nickel = $9.75 \times 10^{-23} \times 6.022 \times 10^{23} = 58.7$ g

∴ Atomic mass = **58.7.**

8. 2 g of hydrogen contain molecules = 6.022×10^{23}

1000 g of hydrogen contain molecules $= \frac{6.022\times10^{23}\times1000}{2} =$ **3.01×10^{26}.**

9. 1 mole of electrons = 6.022×10^{23}

Total charge on 1 mole of electrons = $1.60 \times 10^{-19} \times 6.022 \times 10^{23}$

= **9.64×10^4 C.**

10. Mass of drop of rain = $0.448 \times 1 = 0.448$ g

18 g of water contain molecules = 6.022×10^{23}

0.448 g of water contains molecules $= \frac{6.022\times10^{23}\times0.448}{18}$

= **1.5×10^{22}.**

1 molecule of water = 2 H atoms

No. of hydrogen atoms = $1.5 \times 10^{22} \times 2 =$ **3.0×10^{22} atoms.**

11. Volume of oxygen at N.T.P.

p_1 = 750 mm p_2 =760 mm

V_1 = 150 mL V_2 = ?

T_1 =273 + 20 = 293 K T_2 = 273 K

Applying $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$ or $V_2 = \frac{p_1V_1T_2}{T_1p_2}$

∴ $V_2 = \frac{750\times150\times273}{293\times760} = 137.9$ mL

22400 mL of oxygen at N.T.P. has molecules = 6.022×10^{23}

137.9 mL of oxygen at N.T.P. has molecules $= \frac{6.022\times10^{23}\times137.9}{22400}$

= **3.71×10^{21}.**

12.

Element	Percentage	Atomic mass	Atomic ratio	Simple atomic ratio	Simplest whole no. ratio
M	70	56	$\frac{70}{56} = 1.25$	$\frac{1.25}{1.25} = 1$	2
O	30	16	$\frac{50}{16} = 1.875$	$\frac{1.875}{1.25} = 1.5$	3

Empirical formula = **M_2O_3.**

13. 0.4 moles of $H_3PO_4 \equiv 0.4 \times 3 = 1.2$ mol of H

$\equiv 0.4 \times 1 = 0.4$ mol of P

$\equiv 0.4 \times 4 = 1.6$ mol of O

14. Moles of KOH = $\frac{5.6}{56} = 0.1$

Volume = 250 mL

Molarity = $\frac{0.1}{250} \times 1000 =$ **0.4 M.**

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15. Moles of SO_2 required = $\frac{6.022\times10^{24}}{6.022\times10^{23}}$ = 10 mole

$$S + O_2 \longrightarrow SO_2$$

1 mole of SO_2 is prepared from = 1 gram atom of S

10 mole of SO_2 are prepared from = 10 gram atoms of S

1 mole of SO_2 require O_2 = 32 g

10 mole of SO_2 require O_2 = 32 × 10 = **320 g.**

16. (*a*) 56 g of iron = 1 mole

1.68 g of iron = $\frac{1}{56}$ × 1.68 = **0.03 mol**

(*b*) 1 mole of iron = 6.022×10^{23} atoms

0.03 mole of iron = $6.022 \times 10^{23} \times 0.03 = \mathbf{1.8 \times 10^{22}}$.

17. $2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$

2 (23 + 1 + 12 + 48) = 168 g — 22.4 L at N.T.P.

Volume of CO_2 at N.T.P.

p_1 = 760 mm, p_2 = 760 mm

V_1 = 300 mL, V_2 = ?

T_1 = 273 + 27 = 300 K, T_2 = 273

Applying $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$ or $V_2 = \frac{p_1V_1T_2}{p_2T_1}$

$\therefore$ $V_2 = \frac{760\times300\times273}{760\times300}$ = 273 mL

Calculation of pure $NaHCO_3$

22400 ml of CO_2 at N.T.P. are produced by heating 168 g of $NaHCO_3$

273 ml of CO_2 at N.T.P. are produced by heating

$NaHCO_3 = \frac{168}{22400}\times273 = 2.0475$

Wt. of sample taken = 2.5 g

% Purity = $\frac{2.0475}{2.5}\times100$ = **81.9%.**

18. $KOH + HCl \longrightarrow KCl + H_2O$

56 36.5

56 g of KOH require HCl for neutralisation = 36.5 g

7×10^3 g of KOH require HCl for neutralisation

$= \frac{36.5}{56}\times7\times10^3$

$= 4.56 \times 10^3$ g = 4.56 kg

Wt. of 40% HCl = $\frac{4.56\times100}{40}$ = 11.4 kg

Cost = 11.4 × 6 = ₹ 68.4

$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$

112 g 98 g

112 g of KOH require H_2SO_4 for neutralisation = 98 g

7×10^3 g of KOH require H_2SO_4 for neutralisation

$= \frac{98}{112} \times 7 \times 10^3$ g = 6.125 kg

Wt. of 80% $H_2SO_4 = \frac{6.125\times100}{80}$ = 7.66 kg

Cost = 7.66 × 3.50 = ₹ 26.81

$\therefore$ **It is cheaper to neutralise KOH by H_2SO_4 than HCl.**

19.

Element	Percentage	Atomic mass	Moles of atoms	Mole ratio	Simple whole no. ratio
C	56.8	12	$\frac{50.8}{12}$ = 4.73	$\frac{4.73}{0.59}$ = 8	8
H	6.50	1	$\frac{6.50}{1}$ = 6.50	$\frac{6.50}{0.59}$ = 11	11
O	28.4	16	$\frac{28.4}{16}$ = 1.77	$\frac{1.77}{0.59}$ = 3	3
N	8.28	14	$\frac{8.28}{14}$ = 0.59	$\frac{0.59}{0.59}$ = 1	1

Empirical formula = $\mathbf{C_8H_{11}O_3N}$.

20. 98.0% H_2SO_4 means that 98 g of H_2SO_4 is present in 100 g of solution.

Moles of H_2SO_4 = $\frac{98}{98}$ = 1 mol

Volume of solution = $\frac{100}{1.84}$ = 54.35 mL

Molarity = $\frac{1}{54.35}\times1000$ = **18.4 M**

Now applying molarity equation,

$M_1V_1 = M_2V_2$

$18.4 \times V_1 = 0.20 \times 10.0$L

$\therefore$ $V_1 = \frac{0.20\times10}{18.4}$ = 0.1087L

= **108.7 mL.**

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Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

CONCEPT OF EQUIVALENT MASS

The **equivalent mass of a substance** is defined as *the number of parts by mass of a substance which combines with or displaces directly or indirectly 1.008 parts by mass of hydrogen or 8 parts by mass of oxygen or 35.5 parts by mass of chlorine.*

The following examples clearly illustrate the definition of equivalent mass :

- *Chlorine combines with hydrogen to form hydrogen chloride; HCl as :*

$$\underset{2}{H_2} + \underset{71}{Cl_2} \longrightarrow 2\,HCl$$

Hence, 2 parts by mass of hydrogen combine with 71 parts by mass of chlorine.

or 1 part by mass of hydrogen will combine with 35.5 parts by mass of chlorine.

Hence, **equivalent mass of chlorine is 35.5.**

[For simplicity 1 part by mass of hydrogen may be taken, instead of 1.008 parts]

- *Magnesium wire burns in oxygen gas to form magnesium oxide :*

$$\underset{2\times 24}{Mg} + \underset{32}{O_2} \longrightarrow 2MgO$$

32 parts by mass of oxygen combine with 48 parts by mass of magnesium.

8 parts by mass of oxygen will combine with 12 parts by mass of magnesium.

Hence, **equivalent mass of magnesium is 12.**

- *Zinc metal reacts with dil. H_2SO_4 to liberate hydrogen gas :*

$$\underset{65}{Zn} + \underset{98}{H_2SO_4} \longrightarrow ZnSO_4 + \underset{2}{H_2}$$

2 parts by mass of hydrogen is liberated by 65 parts by mass of zinc.

1 part by mass of hydrogen is liberated by 32.5 parts by mass of zinc.

Hence, **equivalent of mass of zinc = 32.5**

Similarly,

2 parts by mass of hydrogen ≡ 98 parts by mass of H_2SO_4

1 part by mass of hydrogen ≡ 49 parts by mass of H_2SO_4

Hence, **equivalent mass of H_2SO_4 = 49**

Equivalent mass can also be calculated from the formulae of the compounds.

For example :

- **$AlCl_3$:** 3 × 35.5 parts by mass of chlorine combine with 27 parts by mass of Al.

  35.5 parts by mass of chlorine will combine with 9 parts by mass of Al

  ∴ **Equivalent mass of Al = 9**

- **FeO :** 16 parts by mass of oxygen ≡ 56 parts by mass of Fe

  8 parts by mass of oxygen ≡ 28 parts by mass of Fe

  ∴ **Equivalent mass of Fe = 28.**

Gram equivalent mass

The mass of a substance in grams which is numerically equal to its equivalent mass is called **gram equivalent mass** or **one gram equivalent**. It is simply the equivalent mass of a substance expressed in grams. For example, 1 gram equivalent of oxygen is 8 gram because equivalent mass of oxygen is 8.

$$\textbf{Gram-equivalents} = \frac{\textbf{Mass in gm}}{\textbf{Equivalent Mass}}$$

▸ It may be noted that the elements with *variable valency* generally exhibit variable equivalent masses. The equivalent mass of an element is related to its valency as,

$$\text{Equivalent mass} = \frac{\text{Atomic mass}}{\text{Valency}}$$

Since atomic mass of an element is always constant, but its valency may change in different compounds, therefore, its equivalent mass changes with change in valency in its compounds.

Equivalent mass of acids, bases and salts

Equivalent mass of an acid *is the number of parts by mass of it which can give one part by mass of H^+ ions in its aqueous solutions or one part by mass of replaceable hydrogen.*

The number of H^+ ions that one molecule of an acid can give in its aqueous solution is known as its **basicity**.

Therefore,

$$\text{Equivalent mass of an acid} = \frac{\text{Molecular mass}}{\text{Basicity}}$$

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For example,

$HCl \rightleftharpoons H^+ + Cl^-$ Basicity = 1

$$\text{Eq. mass} = \frac{\text{Mol. mass}}{1}$$

$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$ Basicity = 2

$$\text{Eq. mass} = \frac{\text{Mol. mass}}{2}$$

and $H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}$ Basicity = 3

$$\text{Eq. mass} = \frac{\text{Mol. mass}}{3}$$

Equivalent mass of a base *is the number of parts by mass of it which can neutralise one equivalent of an acid or it is the number of parts by mass of it which can furnish one equivalent or 17 parts by mass of OH^- ions* in an aqueous solution.

The number of OH^- ions that one molecule of a base can give in its aqueous solution is called its **acidity**. Therefore,

$$\text{Equivalent mass of a base} = \frac{\text{Molecular mass}}{\text{Acidity}}$$

For example,

$NaOH \rightleftharpoons Na^+ + OH^-$ Acidity = 1

$$\text{Eq. mass} = \frac{\text{Mol. mass}}{1}$$

$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$ Acidity = 2

$$\text{Eq. mass} = \frac{\text{Mol. mass}}{2}$$

$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$ Acidity = 3

$$\text{Eq. mass} = \frac{\text{Mol. mass}}{3}$$

Equivalent mass of a salt

The equivalent mass of a salt is that mass of it which contains one equivalent mass of metal.

$$\text{Equivalent mass of salt} = \frac{\text{Mol. mass of salt}}{\text{Total valency of the metal in the salt}}$$

The total valency of a metal is equal to the valency of the metal ion multiplied by the number of atoms present in the formula of the salt. For example,

Salt	*Valency of metal ion*	*No. of metal atoms*	*Total valency*	*Mol. mass*	*Eq. mass*
NaCl	1	1	$1 \times 1 = 1$	58.5	58.1/1 = 58.5
K_2CO_3	1	2	$1 \times 2 = 2$	138	138/2 = 69
$NaHCO_3$	1	1	$1 \times 1 = 1$	84	84/1 = 84
$CaCO_3$	2	1	$2 \times 1 = 2$	100	100/2 = 50
$FeCl_3$	3	1	$3 \times 1 = 3$	162.5	162.5/3 = 54.2
$Al_2(SO_4)_3$	3	2	$3 \times 2 = 6$	342	342/6 = 57

Equivalent mass of an ion

Equivalent mass of an ion is obtained by dividing the formula mass of the ion with its valency (or charge)

$$\text{Equivalent mass of ion} = \frac{\text{Formula mass}}{\text{Charge on ion}}$$

For example,

$$\text{Equivalent mass of } SO_4^{2-} \text{ ion} = \frac{32 + 4 \times 16}{2} = 48$$

Equivalent mass of oxidising and reducing agent in a reaction

A given substance may have different equivalent masses in various reactions. In a simple way, *the equivalent mass of an oxidising agent is calculated from the number of oxygen atoms it produces and equivalent mass of a reducing agent is calculated from the number of oxygen atoms with which it combines. For example,*

(i) Equivalent mass of $KMnO_4$ in the reaction :

$$2\,KMnO_4 + 3\,H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(O)$$

$2(39 + 55 + 64) = 316$ $\qquad$ 5×16

5×16 parts of oxygen are liberated from $KMnO_4$ = 316 parts

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8 parts of oxygen are liberated from

$$KMnO_4 = \frac{316}{5 \times 16} \times 8 = 31.6$$

∴ **Eq. mass of $KMnO_4$ = 31.6**

(*ii*) *Equivalent mass of $K_2Cr_2O_7$ in the reaction :*

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O)$$

$2 \times 39 + 2 \times 52 + 7 \times 16 = 294$; $3 \times 16 = 48$

48 parts of oxygen are liberated from $K_2Cr_2O_3$ = 294

8 parts of oxygen are liberated from $K_2Cr_2O_7$

$$= \frac{294}{48} \times 8 = 49$$

∴ **Eq. mass of $K_2Cr_2O_7$ = 49**

(*iii*) *Equivalent mass of $FeSO_4$ in the reaction :*

$$2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O$$

$2(56 + 32 + 64) = 304$; 16

16 parts of oxygen react with $FeSO_4$ = 304 parts

8 parts of oxygen react with $FeSO_4 = \frac{304}{16} \times 8 = 152$

∴ **Eq. mass of $FeSO_4$ = 152**

(*iv*) *Equivalent mass of $Na_2S_2O_3$ in the reaction :*

$$2Na_2S_2O_3 + H_2O + O \longrightarrow Na_2S_4O_6 + 2NaOH$$

$2(46 + 64 + 48) = 316$; 16

16 parts of oxygen react with $Na_2S_2O_3$ = 316 parts

8 parts of oxygen react with $Na_2S_2O_3 = \frac{316}{16} \times 8 = 158$

∴ **Eq. mass of $Na_2S_2O_3$ = 158**

DULONG AND PETIT'S LAW

According to Dulong and Petit's law, the product of atomic mass and specific heat for a solid element is approximately equal to 6.4.

Atomic mass × Specific heat = 6.4

This relation can be used to calculate atomic mass.

First approximate atomic mass may be calculated as:

$$\text{Approximate atomic mass} = \frac{6.4}{\text{Specific heat}}$$

From this, valency can be calculated as

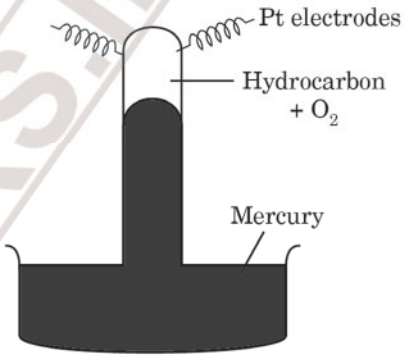
$$\text{Valency} = \frac{\text{Approx. atomic mass}}{\text{Equivalent mass}}$$

Take the valency to nearest whole number, then

Exact atomic mass = Equivalent mass × Valency

EUDIOMETRY

This method has been used for determining the molecular formula or percentage composition of a gaseous mixture of hydrocarbons. The apparatus consists of a closed graduated tube open at one end.



Eudiometer tube

The closed end is provided with platinum electrodes for the passage of electricity through the gas. Such tube is called **eudiometer tube**. It is filled with mercury and inverted over a trough containing mercury. The method involves the following steps:

(*i*) A known volume of the gaseous hydrocarbon or gaseous mixture mixed with excess of oxygen or air is introduced in the eudiometer tube over mercury.

(*ii*) The mixture is exploded by electric spark so that C and H are oxidised to CO_2 and H_2O respectively.

(*iii*) The mixture is then cooled so that water vapour condense to liquid water whose volume is negligible as compared to the volumes of other gases.

(*iv*) KOH is introduced which absorbs CO_2 and only unused O_2 is left. Thus,

decrease in volume on adding KOH = volume of CO_2 produced.

The volume of unused O_2 can be measured by absorbing in alkaline solution of pyrogallol or calculated by difference method.

Eudiometry is based on Avogadro's law which states that equal volumes of all gases under similar

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conditions of temperature and pressure contain equal number of molecules or moles. This means that volume ratio among gases is same as mole ratio at same conditions of temperature and pressure.

The equation for combustion of hydrocarbon is

$$C_xH_y(g) + \left(x + \frac{x}{4}\right) O_2(g) \longrightarrow x\ CO_2(g) + \frac{y}{2} H_2O(l)$$

$$1 \text{ mol} \quad \left(x + \frac{y}{4}\right) \text{ mol} \longrightarrow x \text{ mol} + \frac{y}{2} \text{ mol}$$

$$1 \text{ cc} \quad \left(x + \frac{y}{4}\right) \text{ cc} \longrightarrow x \text{ cc} \quad -$$

Values of x and y can be calculated from the following relations:

Volume of O_2 used per cc of hydrocarbon

$$= \left(x + \frac{y}{4}\right) \text{cc}$$

Volume of CO_2 produced = x cc

Contraction in volume on explosion and cooling

$$= \left[1 + \left(x + \frac{y}{4}\right)\right] - x = \left(1 + \frac{y}{4}\right) \text{cc}$$

Illustration 1. *8.0 mL of a gaseous hydrocarbon was exploded with 45 mL of oxygen. The volume of gases on cooling was found to be 37 mL, 16 mL of which was absorbed by KOH and rest was absorbed in an alkaline solution of pyrogallol. If all volumes are measured under same conditions, deduce the formula of the hydrocarbon.*

Solution.

Volume of CO_2 produced = 16 mL (absorbed by KOH)

Contraction in volume on cooling

$$= 8.0 + 45 - 37 = 16 \text{ mL}$$

Now, volume of CO_2 produced for 1 mL of hydrocarbon

$$= x \text{ mL}$$

Volume of CO_2 produced for 8 mL of hydrocarbon

$$= 8x \text{ mL}$$

$$\therefore \quad 8x = 16 \quad \text{or} \quad x = 2$$

Contraction in volume on cooling for 8 mL of hydrocarbon = $8\left(1 + \frac{y}{4}\right)$

$$\therefore \quad 8\left(1 + \frac{y}{4}\right) = 16 \quad \text{or} \quad 8 + 2y = 16 \quad \text{or} \quad y = 4$$

Hence, formula of compound is C_2H_4.

Illustration 2. *10 mL of a gaseous hydrocarbon was burnt completely in 100 mL of O_2 at NTP. On cooling the gas occupied 80 mL at N.T.P. This volume became 50 mL on treatment with KOH solution. What is the formula of the hydrocarbon?*

Solution. Volume of CO_2 produced + Volume of unreacted O_2 = 80 mL

Volume of unreacted O_2 (CO_2 absorbed by KOH) = 50 mL

Volume of O_2 reacted with 10 mL of hydrocarbon = 100 – 50 = 50 mL

Volume of CO_2 produced by 10 mL of hydrocarbon and 50 mL of O_2 = 80 – 50 = 30 mL

$$C_x H_y(g) + \left(x + \frac{y}{4}\right) O_2(g) \longrightarrow x\ CO_2(g) + \frac{y}{2} H_2O\ (l)$$

Volume of CO_2 produced by 10 mL hydrocarbon,

$$10x = 30$$

$$\therefore \quad x = 3$$

Volume of O_2 reacted with 10 mL hydrocarbon,

$$10\left(x + \frac{y}{4}\right) = 50 \text{ mL}$$

$$x + \frac{y}{4} = 5$$

$$3 + \frac{y}{4} = 5 \text{ or } \frac{y}{4} = 2$$

$$\therefore \quad y = 8$$

Hence, formula of hydrocarbon is C_3H_8.

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OBJECTIVE TYPE QUESTIONS

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Select the Correct Answers :

Matter, Physical Measurements, Laws of Combination

A1. The number of significant figures in 0.0101 is :
(*a*) 3 (*b*) 2
(*c*) 4 (*d*) 5.

A2. Two elements A and B combine to form two compounds in which '*a*' gm of A combines with b_1 and b_2 gm of B respectively. According to law of multiple proportions,
(*a*) $b_1 = b_2$
(*b*) b_1 and b_2 bear a simple whole number ratio
(*c*) a_1 and b_1 bear whole number ratio
(*d*) no relation exists between b_1 and b_2.

A3. Two different oxides of a metal contain 20% and 27% oxygen by weight. This is in accordance with the law of :
(*a*) conservation of mass (*b*) constant composition
(*c*) multiple proportion (*d*) reciprocal proportion.

A4. Two elements X and Y have atomic masses 14 and 16 respectively. They can form a series of five compounds A, B, C, D and E in which for the same amount of X, Y is present in the ratio of 1: 2: 3: 4: 5. If the compound A has 28 parts by weight of X and 16 parts by weight of Y, then compound C will have 24 parts by weight of Y combined with
(*a*) 28 parts by weight of X
(*b*) 14 parts by weight of X
(*c*) 7 parts by weight of X
(*d*) 4.1 parts by weight of X

A5. Two oxides of an element contain 57.1% and 72.7% of oxygen. If the first oxide is MO, the second oxide is :
(*a*) MO (*b*) M_2O
(*c*) MO_3 (*d*) MO_2.

A6. Calculate to the correct number of significant figures: 4.26 – (15.635/5.0)
(*a*) 1.16 (*b*) 1.12
(*c*) 1.2 (*d*) 1.133.

Mole Concept, Atomic Mass and Molecular Mass

A7. Which of the following weighs least ?
(*a*) 2.0 gram mole of CO_2
(*b*) 0.1 mole of sucrose ($C_{12}H_{22}O_{11}$)
(*c*) 1 gram atom of calcium
(*d*) 1.5 mole of water.

A8. Which of the following has maximum number of atoms?
(*a*) 18 g of water (*b*) 16 g of O_2
(*c*) 4.4 g of CO_2 (*d*) 16 g of CH_4.

A9. Which of the following contains more molecules ?
(*a*) 1 g CO_2 (*b*) 1 g N_2
(*c*) 1 g H_2 (*d*) 1 g CH_4.

A10. Which of the following weighs least :
(*a*) 2.24 litres of CO_2 at N.T.P.
(*b*) 6.02×10^{21} molecules of CO_2
(*c*) 1 g of CO_2
(*d*) 6.02×10^{22} atoms of carbon.

A11. The number of atoms present in 0.1 mole of P_4 are :
(*a*) 2.4×10^{23} atoms
(*b*) 6.02×10^{22} atoms
(*c*) same as in 0.2 mole of S_8
(*d*) same as in 3.1 g of phosphorus
(atomic mass of P = 31).

A12. The total number of atoms in 8.5 g of NH_3 is :
(*a*) 9.03×10^{23} (*b*) 3.01×10^{23}
(*c*) 1.204×10^{23} (*d*) 6.02×10^{23}

A13. The number of atoms of oxygen present in 11.2 L of ozone at N.T.P. are :
(*a*) 3.01×10^{22} (*b*) 6.02×10^{23}
(*c*) 9.03×10^{24} (*d*) 1.20×10^{24}.

A14. The number of atoms of He in 104 a.m.u. is :
(*a*) 3.1×10^{25} (*b*) 6.2×10^{25}
(*c*) 26 (*d*) 206.

A15. The number of water molecules present in a drop of water weighing 0.018 g is :
(*a*) 6.02×10^{26} (*b*) 6.02×10^{23}
(*c*) 6.02×10^{20} (*d*) 6.02×10^{19}.

A16. 34.2 g of sucrose ($C_{12}H_{22}O_{11}$) are dissolved in 90 g of water in a glass. The number of oxygen atoms in the solution are :
(*a*) 3.66×10^{26} (*b*) 6.6×10^{23}
(*c*) 3.66×10^{24} (*d*) 6.0×10^{22}.

A17. 1 mole of methane contains :
(*a*) 6.02×10^{23} atoms of H
(*b*) 4 gram atoms of hydrogen
(*c*) 1.81×10^{23} molecules of methane
(*d*) 3.0 g of carbon.

A18. The molar masses of oxygen and sulphur dioxide are 32 and 64 respectively. If 1 L of oxygen at 25°C and 750 mm Hg pressure contains N molecules, then the number of molecules in 2 L sulphur dioxide under same conditions of temperature and pressure is :
(*a*) N/2 (*b*) 3N/2 (*c*) 2N (*d*) 6 N.

Answers

A1. (*a*) **A2.** (*b*) **A3.** (*c*) **A4.** (*b*) **A5.** (*d*) **A6.** (*c*) **A7.** (*d*) **A8.** (*d*) **A9.** (*c*) **A10.** (*b*) **A11.** (*a*)
A12. (*a*) **A13.** (*c*) **A14.** (*c*) **A15.** (*c*) **A16.** (*c*) **A17.** (*b*) **A18.** (*c*)

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A19. Which of the following contain highest number of atoms ?
(*a*) 1.0 g of water (*b*) 1.0 g of silver
(*c*) 1.0 g of nitrogen (*d*) 1.0 g of propane (C_3H_8).

A20. Which of the following has maximum mass ?
(*a*) 1.0 mole of H_2 gas
(*b*) 0.5 mole of sucrose ($C_{12}H_{22}O_{11}$)
(*c*) 1.2 mole of silver
(*d*) 22.4 L of N_2 at N.T.P.

A21. Number of molecules present in 1 ml of water is :
(*a*) 1 (*b*) 1000
(*c*) 2.69×10^{19} (*d*) 6.02×10^{20}.

A22. 2 g of oxygen contain number of atoms equal to that contained by :
(*a*) 0.5 g hydrogen (*b*) 4 g sulphur
(*c*) 7 g nitrogen (*d*) 2.3 g sodium.

A23. 40 g of caustic soda contain :
(*a*) 6.02×10^{23} atoms of H
(*b*) 22.4 litres of N_2
(*c*) 6.02×10^{24} molecules of O_2
(*d*) 4 g of Na.

A24. 0.6 g of carbon was burnt in air to form CO_2. The number of molecules of CO_2 introduced into air will be :
(*a*) 6.02×10^{22} (*b*) 3.01×10^{22}
(*c*) 6.023×10^{23} (*d*) 3.01×10^{23}.

A25. The total number of electrons present in 3.2 g of methane are :
(*a*) $2 \times 10 \times 6.022 \times 10^{22}$ (*b*) $10 \times 6.022 \times 10^{23}$
(*c*) $10 \times 6.022 \times 10^{22}$ (*d*) 6.022×10^{23}.

A26. The number of atoms in 4.25 g of NH_3 is approximately
(*a*) 1×10^{23} (*b*) 2×10^{23}
(*c*) 4×10^{23} (*d*) 6×10^{23}

A27. Haemoglobin contains 0.33% of iron by weight. The molecular mass of haemoglobin is about 67200. The number of iron atoms (at mass of Fe = 56) present in one molecule of haemoglobin is
(*a*) 6 (*b*) 4 (*c*) 2 (*d*) 1

A28. How many moles of electron weigh one kilogram ?
(*a*) 6.022×10^{23} (*b*) $\frac{1}{9.108} \times 10^{31}$
(*c*) $\frac{6.022}{9.108} \times 10^{54}$ (*d*) $\frac{1}{9.108 \times 6.022} \times 10^{8}$

A29. An alkaloid contains 17.28% of nitrogen and its molecular mass is 162. The number of nitrogen atoms present in one molecule of alkaloid is
(*a*) five (*b*) four
(*c*) three (*d*) two

A30. Number of atoms in 558.6 g Fe (atomic mass of Fe = 55.86 g mol^{-1}) is
(*a*) twice that in 60 g carbon
(*b*) 6.023×10^{22}
(*c*) half that of 8 g He
(*d*) $558.6 \times 6.023 \times 10^{23}$

Percentage Composition, Molecular formula and Stoichiometry

A31. The empirical formula of sucrose is :
(*a*) CH_2O (*b*) CHO
(*c*) $C_{12}H_{22}O_{11}$ (*d*) $C(H_2O)_2$.

A32. One mole of calcium phosphide on reaction with excess of water gives
(*a*) One mole of phosphine
(*b*) Two moles of phosphoric acid
(*c*) Two moles of phosphine
(*d*) One mole of phosphorus pentoxide

A33. A sample of water contains *x* % of D_2O. Its molecular weight is 19. The value of '*x*' is
(*a*) 25 (*b*) 50 (*c*) 33.33 (*d*) 75

A34. A compound contains 8% sulphur. The minimum molecular weight of the compound is
(*a*) 100 (*b*) 200 (*c*) 350 (*d*) 400

A35. An aqueous solution of 6.3 g of oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 N NaOH required to completely neutralize 10 mL of this solution is :
(*a*) 40 mL (*b*) 20 mL
(*c*) 10 mL (*d*) 5 mL

A36. Mixture X = 0.02 mol of $[Co(NH_3)_5SO_4]Br$ and 0.02 mol of $[Co(NH_3)_5Br]SO_4$ was prepared in 2 L of solution :
1 L of mixture X + excess of $AgNO_3 \longrightarrow$ Y
1 L of mixture X + excess of $BaCl_2 \longrightarrow$ Z
Number of moles of Y and Z are :
(*a*) 0.01, 0.01 (*b*) 0.02, 0.01
(*c*) 0.01, 0.02 (*d*) 0.02, 0.02

A37. In Haber process, 30 L of dihydrogen and 30 L of dinitrogen were taken for reaction which yielded only 50% of the expected product. What will be the composition of the gaseous mixture under the aforesaid conditions in the end ?
(*a*) 20 L NH_3, 25 L N_2 and 20 L H_2
(*b*) 10 L NH_3, 25 L N_2 and 15 L H_2
(*c*) 20 L NH_3, 10 L N_2 and 30 L H_2
(*d*) 20 L NH_3, 25 L N_2 and 15 L H_2

A38. A gaseous mixture contains 50% He and 50% CH_4 by volume. What is the percent by weight of CH_4 in the mixture ?
(*a*) 19.97% (*b*) 20.05%
(*c*) 50% (*d*) 80.03%

Answers

A19. (*d*) **A20.** (*b*) **A21.** (*c*) **A22.** (*b*) **A23.** (*a*) **A24.** (*b*) **A25.** (*a*) **A26.** (*d*) **A27.** (*b*) **A28.** (*d*) **A29.** (*d*) **A30.** (*a*) **A31.** (*c*) **A32.** (*c*) **A33.** (*b*) **A34.** (*d*) **A35.** (*a*) **A36.** (*a*) **A37.** (*b*) **A38.** (*d*)

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A39. The mass of carbon anode consumed (giving only carbon dioxide) in the production of 270 kg of aluminium metal from bauxite by Hall process is :
(a) 180 kg (b) 270 kg
(c) 540 kg (d) 90 kg

A40. The crystalline salt $Na_2SO_4.xH_2O$ on heating loses 55.9 % of its weight. The formula of crystalline salt is
(a) $Na_2SO_4.5H_2O$ (b) $Na_2SO_4.7H_2O$
(c) $Na_2SO_4.2H_2O$ (d) $Na_2SO_4 . 10H_2O$

A41. 20 kg of $N_2(g)$ and 3.0 kg of $H_2(g)$ are mixed to produce $NH_3(g)$. The amount of $NH_3(g)$ formed is
(a) 17 kg (b) 51 kg
(c) 60 kg (d) 34 kg

A42. A phosphorus oxide has 43.6% phosphorus (at. mass = 31). The empirical formula of the compound is
(a) P_2O_5 (b) P_4O_6
(c) P_2O_3 (d) P_4O_8

A43. Commercially available concentrated HCl contains 38·0% HCl by mass (density = 1·19 g mL^{-1}). The molarity of the solution is
(a) 10·40 M (b) 5·70 M
(c) 12·38 M (d) 13·46 M

A44. The molarity of a solution obtained by mixing 800 mL of 0.5 M HCl with 200 mL of 1 M HCl will be
(a) 0.8 M (b) 0.6 M
(c) 0.4 M (d) 0.2 M

A45. 4L of water is added to 2L of 6M HCl. The molarity of the final solution is
(a) 4 M (b) 2 M
(c) 1 M (d) 0·5 M

A46. The volume of 10.50 M solution required to prepare 1.0 L of 0.25 M solution of HNO_3 is :
(a) 250 mL (b) 500 mL
(c) 230 mL (d) 23.8 mL.

A47. The moles of sodium chloride in 250 cm^3 of 0.50 M NaCl are :
(a) 0.250 mol (b) 2 mol
(c) 0.125 mol (d) 1.0 mol.

A48. 6 mL of a gaseous hydrocarbon was exploded with excess of oxygen and the product cooled. A contraction of 9 mL was observed. A further contraction of 12 mL was observed on treatment with aqueous KOH. The formula of hydrocarbon is
(a) CH_4 (b) C_2H_4
(c) C_2H_6 (d) C_2H_2

Answers

A39. (d) **A40.** (d) **A41.** (a) **A42.** (a) **A43.** (c) **A44.** (b) **A45.** (b) **A46.** (d) **A47.** (c) **A48.** (d)

B MULTIPLE CHOICE QUESTIONS *from Competitive Examinations*

AIPMT & Other State Boards' Medical Entrance

B1. What volume of oxygen gas (O_2) measured at 0°C and 1 atm, is needed to burn completely 1 L of propane gas (C_3H_8) measured under the same conditions?
(a) 6 L (b) 5 L
(c) 10 L (d) 7 L
(C.B.S.E. PMT 2008)

B2. How many moles of lead (II) chloride will be formed from a reaction between 6.5 g of PbO and 3.2 g of HCl?
(a) 0.333 (b) 0.011
(c) 0.029 (d) 0.044
(C.B.S.E. PMT 2008)

B3. Volume occupied by one molecule of water (density = 1 g cm^{-3}) is :
(a) 6.023×10^{-23} cm^3 (b) 3.0×10^{-23} cm^3
(c) 5.5×10^{-23} cm^3 (d) 9.0×10^{-23} cm^3
(C.B.S.E. PMT 2008)

B4. Which of the following concentration terms is/are independent of temperature ?
(a) Molality only
(b) Molality and mole fraction
(c) Molarity and mole fraction
(d) Molality and normality
(e) Molarity only *(Kerala PMT 2009)*

B5. 10 g of hydrogen and 64 g of oxygen were filled in a steel vessel and exploded. Amount of water produced in this reaction will be
(a) 3 mol (b) 4 mol
(c) 1 mol (d) 2 mol
(C.B.S.E. PMT. 2009)

B6. The number of molecules in 100 ml of 0.02 N H_2SO_4 is
(a) 6.02×10^{22} (b) 6.02×10^{21}
(c) 6.02×10^{20} (d) 6.02×10^{18}
(AMU Med. 2010)

B7. If 1.5 moles of oxygen combine with Al to form Al_2O_3, the mass of Al in g [Atomic mass of Al = 27] used in the reaction is
(a) 2.7 (b) 54
(c) 40.5 (d) 81
(e) 27 *(Kerala PMT 2010)*

B8. For a reaction A + 2B → C, the amount of C formed by starting the reaction with 5 moles of A and 8 moles of B is
(a) 5 moles (b) 8 moles
(c) 16 moles (d) 4 moles
(e) 1 mole *(Kerala PMT 2010)*

B9. One kilogram of a sea water sample contains 6 mg of dissolved O_2. The concentration of O_2 in the sample in ppm is
(a) 0.6 (b) 6.0
(c) 60.0 (d) 16.0
(e) 32.0 *(Kerala PMT 2010)*

Answers

B1. (b) **B2.** (c) **B3.** (b) **B4.** (b) **B5.** (b) **B6.** (c) **B7.** (b) **B8.** (d) **B9.** (b)

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B10. 25.3 g of sodium carbonate, Na_2CO_3 is dissolved in enough water to make 250 mL of solution. If sodium carbonate dissociates completely, molar concentration of Na^+ and CO_3^{2-} ions are respectively (molar mass of Na_2CO_3 = 106 g mol^{-1})

(*a*) 0.477 M and 0.477 M

(*b*) 0.955 M and 1.910 M

(*c*) 1.910 M and 0.955 M

(*d*) 1.90 M and 1.910 M *(C.B.S.E PMT 2010)*

B11. The number of atoms in 0.1 mol of triatomic gas is ($N_A = 6.02 \times 10^{23}$)

(*a*) 1.800×10^{22} (*b*) 6.026×10^{22}

(*c*) 1.806×10^{23} (*d*) 3.600×10^{22} *(C.B.S.E. PMT 2010)*

B12. Which one of the following sets of compounds correctly illustrate the law of reciprocal proportions ?

(*a*) P_2O_3, PH_3, H_2O (*b*) P_2O_5, PH_3, H_2O

(*c*) N_2O_5, NH_3, H_2O (*d*) N_2O, NH_3, H_2O

(*e*) NO_2, NH_3, H_2O *(Kerala P.M.T. 2011)*

B13. 20.0 kg of N_2(g) and 3.0 kg of H_2(g) are mixed to produce NH_3(g). The amount of NH_3(g) formed is

(*a*) 17 kg (*b*) 34 kg

(*c*) 20 kg (*d*) 3 kg

(*e*) 23 kg *(Kerala P.M.T. 2011)*

B14. Mole fraction of the solute in a 1.00 molal aqueous solution is

(*a*) 0.1770 (*b*) 0.0177

(*c*) 0.0344 (*d*) 1.7700 *(A.I.P.M.T. 2011)*

B15. What is the volume of CO_2 liberated (in litres) at 1 atmosphere and 0°C when 10 g of 100% pure calcium carbonate is treated with excess dilute sulphuric acid? (Atomic mass Ca = 40, C = 12, O = 16)

(*a*) 0.224 (*b*) 2.24

(*c*) 22.4 (*d*) 224

(*e*) 11.2 *(Kerala P.M.T. 2012)*

B16. Which one of the following is the lightest ?

(*a*) 0.2 mole of hydrogen gas.

(*b*) 6.023×10^{22} molecules of nitrogen.

(*c*) 0.1 g of silver.

(*d*) 0.1 mole of oxygen gas.

(*e*) 1 g of water. *(Kerala P.M.T. 2012)*

B17. When 22.4 litres of $H_2(g)$ is mixed with 11.2 litres of $Cl_2(g)$, each at S.T.P, the moles of HCl(g) formed is equal to

(*a*) 1 mol of HCl(g) (*b*) 2 mol of HCl(g)

(*c*) 0.5 mol of HCl(g) (*d*) 1.5 mol of HCl(g) *(AIPMT 2014)*

B18. 1.0 g of magnesium is burnt with 0.56 g O_2 in a closed vessel. Which reactant is left in excess and how much? (At. wt. Mg = 24, O = 16)

(*a*) Mg, 0.16 g (*b*) O_2, 0.16 g

(*c*) Mg, 0.44 g (*d*) O_2, 0.28 g *(AIPMT 2014)*

B19. The mass of $CaCO_3$ required to react completely with 20 mL of 1.0 M HCl as per the reaction:

$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$ is

(At. mass: Ca = 40, C = 12, O = 16)

(*a*) 1 g (*b*) 2 g

(*c*) 10 g (*d*) 20 g

(*e*) 200 g *(Kerala PMT 2015)*

B20. Which one of the following has maximum number of molecules?

(*a*) 16 g of O_2 (*b*) 16 g of NO_2

(*c*) 4 g of N_2 (*d*) 2 g of H_2

(*e*) 32 g of N_2 *(Kerala PMT 2015)*

B21. A mixture of gases contains H_2 and O_2 gases in the ratio of 1 : 4 (w/w). What is the molar ratio of the two gases in the mixture?

(*a*) 16 : 1 (*b*) 2 : 1

(*c*) 1 : 4 (*d*) 4 : 1 *(A.I.P.M.T. 2015)*

B22. If Avogadro number N_A is changed from 6.022×10^{23} mol^{-1} to 6.022×10^{20} mol^{-1}, this would change:

(*a*) the ratio of chemical species to each other in a balanced equation.

(*b*) the ratio of elements to each other in a compound.

(*c*) the definition of mass in units of grams.

(*d*) the mass of one mole of carbon. *(A.I.P.M.T. 2015)*

B23. The number of water molecules is maximum in:

(*a*) 18 gram of water

(*b*) 18 moles of water

(*c*) 18 molecules of water.

(*d*) 1.8 gram of water. *(A.I.P.M.T. 2015)*

B24. 20.0 g of a magnesium carbonate sample decomposes on heating to give carbon dioxide and 8.0 g magnesium oxide. What will be the percentage purity of magnesium carbonate in the sample?

(*a*) 60 (*b*) 84

(*c*) 75 (*d*) 96 *(A.I.P.M.T. 2015)*

B25. What is the mole fraction of the solute in a 1.00 m aqueous solution?

(*a*) 0.0354 (*b*) 0.0177

(*c*) 0.177 (*d*) 1.770 *(A.I.P.M.T. 2015)*

Answers

B10. (*c*) **B11.** (*c*) **B12.** (*a*) **B13.** (*a*) **B14.** (*b*) **B15.** (*b*) **B16.** (*c*) **B17.** (*a*) **B18.** (*a*) **B19.** (*a*)
B20. (*e*) **B21.** (*d*) **B22.** (*d*) **B23.** (*b*) **B24.** (*b*) **B25.** (*b*)

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B26. What is the mass of the precipitate formed when 50 mL of 16.9% solution of $AgNO_3$ is mixed with 50 mL of 5.8% NaCl solution?
(Ag = 107.8, N = 14, O = 16, Na = 23, Cl = 35.5)
(a) 7 g (b) 14 g
(c) 28 g (d) 3.5 g
(A.I.P.M.T. 2015)

B27. Suppose the elements X and Y combine to form two compounds XY_2 and X_3Y_2. When 0.1 mole of XY_2 weighs 10 g and 0.05 mole of X_3Y_2 weighs 9 g, the atomic weights of X and Y are
(a) 40, 30 (b) 60, 40
(c) 20, 30 (d) 30, 20 *(NEET 2016)*

B28. Which of the following is dependent on temperature?
(a) Molality (b) Molarity
(c) Mole fraction (d) Weight percentage
(NEET 2017)

B29. In which case is number of molecules of water maximum?
(a) 18 mL of water
(b) 0.18 g of water
(c) 0.00224 L of water vapours at 1 atm and 273 K
(d) 10^{-3} mol of water *(NEET 2018)*

JEE (Main) & Other State Boards' Engineering Entrance

B30. If we consider that 1/6 in place of 1/12 mass of carbon atom is taken to be the relative atomic mass unit, the mass of one mole of a substance will
(a) decrease twice
(b) increase two fold
(c) remain unchanged
(d) be a fraction of molecular mass of the substance
(A.I.E.E.E. 2005)

B31. In the reaction :
$2\,Al(s) + 6HCl\,(aq) \longrightarrow 2Al^{3+}\,(aq) + 6Cl^{-}\,(aq) + 3H_2(g)$
(a) 33.6 L $H_2(g)$ is produced regardless of temperature and pressure for every mole of Al that reacts.
(b) 67.2 L $H_2(g)$ at STP is produced for every mole of Al that reacts.
(c) 11.2 L H_2 (g) at STP is produced for every mole of HCl (aq) consumed.
(d) 6 L HCl (aq) is consumed for every 3 L of $H_2(g)$ is produced. *(A.I.E.E.E. 2007)*

B32. 80 g of oxygen contain as many atoms as in
(a) 10 g of hydrogen
(b) 5 g of hydrogen
(c) 80 g of hydrogen
(d) 1 g of hydrogen *(Karnataka C.E.T. 2008)*

B33. What is the molality of pure water?
(a) 1 (b) 18
(c) 55.5 (d) None of these
(Orissa JEE 2008)

B34. The volume of 10N and 4 N HCl required to make 1 L of 7 N HCl are
(a) 0.50 L of 10 N HCl and 0.50 L of 4 N HCl
(b) 0.60 L of 10 N HCl and 0.40 L of 4 N HCl
(c) 0.80 L of 10 N HCl and 0.20 L of 4 N HCl
(d) 0.75 L of 10 N HCl and 0.25 L of 4 N HCl
(Orissa J.E.E. 2009)

B35. The molarity of 98% H_2SO_4 (d = 1.8 g/mL) by weight is
(a) 6 M (b) 18 M
(c) 10 M (d) 4 M *(MP-PET 2009)*

B36. 20 mL of 10 N HCl are mixed with 10 mL of 36 N H_2SO_4 and the mixture is made 1L. Normality of the mixture will be
(a) 0.56 N (b) 0.50 N
(c) 0.40 N (d) 0.35 N
(MP-PET 2009)

B37. Excess of carbon dioxide is passed through 50 mL of 0.5 M calcium hydroxide solution. After the completion of the reaction, the solution was evaporated to dryness. The solid calcium carbonate was completely neutralised with 0.1 N hydrochloric acid. The volume of hydrochloric acid required is
(a) 200 cm^3 (b) 500 cm^3
(c) 400 cm^3 (d) 300 cm^3
(Karnataka C.E.T. 2009)

B38. How much time (in hours) would it take to distribute one Avogadro number of wheat grains if 10^{20} grains are distributed each second ?
(a) 0.1673 (b) 1.673
(c) 16.73 (d) 167.3
(e) 1673 *(Kerala PET 2010)*

B39. Two oxides of a metal contain 36.4% and 53.4% of oxygen by mass respectively. If the formula of the first oxide is M_2O, then that of the second is
(a) M_2O_3 (b) MO
(c) MO_2 (d) M_2O_5
(J.K. C.E.T. 2011)

B40. Arrange the following in the order of increasing mass (atomic mass : O = 16, Cu = 63, N = 14)
I. one atom of oxygen
II. one atom of nitrogen
III. 1×10^{-10} mole of oxygen
IV. 1×10^{-10} mole of copper
(a) II < I < III < IV (b) I < II < III < IV
(c) III < II < IV < I (d) IV < II < III < I
(e) II < IV < I < III
(Kerala P.E.T. 2011)

Answers

B26. (a) **B27.** (a) **B28.** (b) **B29.** (a) **B30.** (a) **B31.** (c) **B32.** (b) **B33.** (c) **B34.** (a) **B35.** (b)
B36. (a) **B37.** (b) **B38.** (b) **B39.** (b) **B40.** (a)

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B41. A mixture of ethane and ethene occupies 41 L at 1 atm and 500 K. The mixture reacts completely with $\frac{10}{3}$ mole of O_2 to produce CO_2 and H_2O. The mole fractions of ethane and ethene in the mixture are (R = 0.082 L atm K^{-1} mol^{-1}) respectively
(a) 0.50, 0.50 (b) 0.75, 0.25
(c) 0.67, 0.33 (d) 0.25, 0.75
(e) 0.33, 0.67 *(Kerala P.E.T. 2011)*

B42. A mixture of $CaCl_2$ and NaCl weighing 4.44 g is treated with sodium carbonate solution to precipitate all the calcium ions as calcium carbonate. The calcium carbonate so obtained is heated strongly to get 0.56 g of CaO.
The percentage of NaCl in the mixture is [Atomic mass of Ca = 40]
(a) 31.5 (b) 75
(c) 25 (d) 40.2
(Karnataka C.E.T. 2011)

B43. 50 cm^3 of 0.2 N HCl is titrated against 0.1 N NaOH solution. The titration was discontinued after adding 50 cm^3 of NaOH. The remaining titration is completed by adding 0.5 N KOH. The volume of KOH required for completing the titration is
(a) 10 cm^3 (b) 12 cm^3
(c) 16.2 cm^3 (d) 21.0 cm^3
(Karnataka C.E.T. 2011)

B44. A 100% pure sample of a divalent metal carbonate weighing 2 g on complete thermal decomposition releases 448 cc of carbon dioxide at STP. The equivalent mass of the metal is
(a) 40 (b) 20
(c) 28 (d) 12
(e) 56 *(Kerala P.E.T. 2012)*

B45. The total number of electrons in 18 mL of water (density = 1 g mL^{-1}) is
(a) 6.02×10^{23} (b) 6.02×10^{25}
(c) 6.02×10^{24} (d) $6.02 \times 18 \times 10^{23}$
(Karnataka C.E.T. 2012)

B46. Two solutions of HCl, A and B, have concentrations of 0.5 M and 0.1 M respectively. The volume of solutions A and B required to make 2 litres of 0.2 M HCl are
(a) 0.5 L of A + 1.5 L of B
(b) 1.5 L of A + 0.5 L of B
(c) 1.0 L of A + 1.0 L of B
(d) 0.75 L of A + 1.25 L of B *(A.M.U. Engg. 2012)*

B47. The number of water molecules present in a drop of water weighing 0.018 g is
(a) 6.022×10^{26} (b) 6.022×10^{23}
(c) 6.022×10^{19} (d) 6.022×10^{20}
(Karnataka CET 2013)

B48. How many grams of concentrated nitric acid solution should be used to prepare 250 mL of 2.0 $MHNO_3$? The concentrated acid is 70% HNO_3.
(a) 70.0 g conc. HNO_3
(b) 54.0 g conc. HNO_3
(c) 45.0 g conc. HNO_3
(d) 90.0 g conc. HNO_3 *(J.K. CET 2013)*

B49. The molarity of a solution obtained by mixing 750mL of 0.5 M HCl with 250 mL of 2 M HCl will be
(a) 0.975 M (b) 0.875 M
(c) 1.00 M (d) 1.75 M
(JEE Main 2013)

B50. A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of CO_2. The empirical formula of the hydrocarbon is
(a) C_7H_8 (b) C_2H_4
(c) C_3H_4 (d) C_6H_6 *(JEEMain2013)*

B51. 10 g of a mixture of BaO and CaO requires 100 cm^3 of 2.5M HCl to react completely. The percentage of calcium oxide in the mixture is approximately (Given molar mass of BaO = 153, CaO = 56).
(a) 52.6 (b) 55.1
(c) 44.9 (d) 47.4
(KarnatakaCET2014)

B52. 25 cm^3 of oxalic acid completely neutralised 0.064 g of sodium hydroxide. Molarity of oxalic acid solution is
(a) 0.064 (b) 0.045
(c) 0.015 (d) 0.032
(KarnatakaCET2014)

B53. A 5.82 g silver coin is dissolved in nitric acid. When sodium chloride is added to the solution, all the silver is precipitated as AgCl. The AgCl precipitate weighs 7.20 g. The percentage of silver in the coin is
(a) 60.3% (b) 80%
(c) 93.1% (d) 70%
(A.M.U. Egg. 2014)

B54. 25 mL of 3.0 M HCl are mixed with 75 mL of 4.0 M HCl. If the volumes are additive, the molarity of the final mixture will be
(a) 4.0 M (b) 3.75 M
(c) 4.25 M (d) 3.50 M
(A.M.U. Egg. 2014)

B55. The ratio of masses of oxygen and nitrogen in a particular gaseous mixture is 1 : 4. The ratio of number of their molecules is
(a) 3 : 16 (b) 1 : 4
(c) 7 : 32 (d) 1 : 8 *(JEEMain2014)*

B56. The number of Cl^- ions in 100 mL of 0.001 M HCl solution is
(a) 6.022×10^{23} (b) 6.022×10^{20}
(c) 6.022×10^{19} (d) 6.022×10^{24}
(A.M.U. Engg 2015)

Answers

B41. (c) **B42.** (b) **B43.** (a) **B44.** (b) **B45.** (c) **B46.** (a) **B47.** (d) **B48.** (c) **B49.** (b) **B50.** (a)
B51. (a) **B52.** (d) **B53.** (c) **B54.** (b) **B55.** (c) **B56.** (c)

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B57. 0.30 g of an organic compound containing C, H and O on combustion yields 0.44 g CO_2 and 0.18 g H_2O. If one mol of compound weighs 60, then molecular formula of the compound is
(a) C_3H_8O (b) $C_2H_4O_2$
(c) CH_2O (d) C_4H_6O
(Karnataka CET 2015)

B58. What amount of dioxygen (in gram) contains 1.8×10^{22} molecules?
(a) 0.960 (b) 96.0
(c) 0.0960 (d) 9.60
(Karnataka CET 2015)

B59. If 27g of water is formed during complete combustion of pure propene (C_3H_6), the mass of propene burnt is
(a) 42 g (b) 21 g
(c) 14 g (d) 56 g
(e) 40 g *(Kerala PET 2016)*

B60. When 2.46 g of a hydrated salt ($MSO_4 . xH_2O$) is completely dehydrated, 1.20 g of anhydrous salt is obtained. If the molecular weight of anhydrous salt is 120 g mol^{-1}, what is the value of x?
(a) 2 (b) 4
(c) 5 (d) 6
(e) 7 *(Kerala PET 2016)*

B61. Calculate the molality of a solution that contains 51.2g of naphthalene, ($C_{10}H_8$) in 500 mL of carbon tetrachloride. The density of CCl_4 is 1.60 g/mL.
(a) 0.250 m (b) 0.500 m
(c) 0.750 m (d) 0.840 m
(e) 1.69 m *(Kerala PET 2016)*

B62. The number of oxygen atoms in 4.4 g of CO_2 is
(a) 1.2×10^{23} (b) 6×10^{22}
(c) 6×10^{23} (d) 12×10^{23}
(Karnataka CET 2016)

B63. An organic compound contains C = 40%, H = 13.33% and N = 46.67%. Its empirical formula is
(a) C_2H_2N (b) C_3H_7N
(c) CH_4N (d) CHN
(Karnataka CET 2016)

B64. At 300 K and 1 atm, 15 mL of a gaseous hydrocarbon requires 375 mL air containing 20% O_2 by volume for complete combustion. After combustion the gases occupy 330 mL. Assuming that the water formed is in liquid form and the volumes were measured at the same temperature and pressure the formula of the hydrocarbon is
(a) C_3H_6 (b) C_3H_8
(c) C_4H_8 (d) C_4H_{10}
(JEE Main 2016)

B65. You are supplied with 500 mL each of 2 N HCl and 5N HCl. What is the maximum volume of 3 M HCl that you can prepare using only these two solutions?
(a) 250 mL (b) 500 mL
(c) 750 mL (d) 1000 mL
(WB-JEE 2017)

B66. 0.126 g of an acid is needed to completely neutralise 20 mL of 0.1 NaOH solution. The equivalent weight of the acid is
(a) 53 (b) 40
(c) 45 (d) 63 *(WB-JEE 2017)*

B67. In a flask, the weight ratio of CH_4(g) and SO_2(g) at 298 K and 1 bar is 1 : 2. The ratio of the number of molecules of $SO_2(g)$ and $CH_4(g)$ is
(a) 1 : 4 (b) 4 : 1
(c) 1 : 2 (d) 2 : 1 *(WB-JEE 2017)*

B68. What will be the normality of the salt solution obtained by neutralizing x mL of y (N) HCl with y mL of x (N) NaOH and finally adding $(x + y)$ mL distilled water ?
(a) $\frac{2(x+y)}{xy}$ N (b) $\frac{xy}{2(x+y)}$ N
(c) $\left(\frac{2xy}{x+y}\right)$ N (d) $\left(\frac{x+y}{xy}\right)$ N
(WB-JEE 2017)

B69. If 3.01×10^{20} molecules are removed from 98 mg of H_2SO_4, then number of moles of H_2SO_4 left are
(a) 0.5×10^{-3} mol (b) 0.1×10^{-3} mol
(c) 9.95×10^{-2} mol (d) 1.66×10^{-3} mol
(Karnataka CET 2017)

B70. 10 g of $MgCO_3$ decomposes on heating to 0.1 mole CO_2 and 4 g MgO. The percent purity of $MgCO_3$ is
(a) 24% (b) 44%
(c) 54% (d) 74%
(e) 84% *(Kerala PET 2017)*

B71. The compound $Na_2CO_3 . x H_2O$ has 50% H_2O by mass. The value of 'x' is
(a) 4 (b) 5
(c) 6 (d) 7
(c) 8 *(Kerala PET 2017)*

B72. 1 gram of a carbonate (M_2CO_3) on treatment with excess HCl produces 0.01186 mole of CO_2. The molar mass of M_2CO_3 in g mol^{-1} is
(a) 1186 (b) 84.3
(c) 118.6 (d) 11.86
(Kerala PET 2017)

B73. Calculate the molarity of a solution of 30 g of $Co(NO_3)_2.6H_2O$ in 4.3 L of solution? Consider atomic mass of Co = 59u, N = 14u, O = 16u, H = 1u.
(a) 0.023 M (b) 0.23 M
(c) 0.046 M (d) 0.46 M
(J.K. CET 2018)

Answers

B57. (b) **B58.** (a) **B59.** (b) **B60.** (e) **B61.** (b) **B62.** (a) **B63.** (c) **B64.** (b) **B65.** (c) **B66.** (d)
B67. (c) **B68.** (b) **B69.** (a) **B70.** (e) **B71.** (c) **B72.** (b) **B73.** (a)

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B74. How many moles of electrons will weigh one kilogram?

(a) 6.023×10^{23} (b) $\frac{1}{9.108} \times 10^{21}$

(c) $\frac{6.023}{9.108} \times 10^{54}$ (d) $\frac{1}{9.108 \times 6.023} \times 10^{8}$

(WB JEE 2018)

B75. A metal M (specific heat 0.16) forms a metal chloride with a 65% chlorine present in it. The formula of the metal chloride will be

(a) MCl (b) MCl_2

(c) MCl_3 (d) MCl_4

(WB JEE 2018)

B76. 1.0 g of Mg is burnt with 0.28 g of O_2 in a closed vessel. Which reactant is left in excess and how much?

(a) Mg, 5.8 g (b) Mg, 0.58 g

(c) O_2, 0.24 g (d) O_2, 2.4 g

(Karnataka CET 2018)

B77. 1 mol of $FeSO_4$ (atomic weight of Fe is 55.84 g mol^{-1}) is oxidised to $Fe_2(SO_4)_3$. Calculate the equivalent weight of ferrous ion.

(a) 55.84 (b) 27.92

(c) 18.61 (d) 111.68

(e) 83.76 *(Kerala PET 2018)*

B78. Mass % of carbon in ethanol is

(a) 52 (b) 13

(c) 34 (d) 90

(e) 80 *(Kerala PET 2018)*

B79. The ratio of mass percent of C and H of an organic compound ($C_xH_yO_z$) is 6 : 1. If one molecule of the above compound ($C_xH_yO_z$) contains half as much oxygen as required to burn one molecule of compound C_xH_y completely to CO_2 and H_2O, the empirical formula of compound $C_xH_yO_z$ is :

(a) $C_3H_6O_3$ (b) C_2H_4O

(c) $C_3H_4O_2$ (d) $C_2H_4O_3$

(JEE Main 2018)

B80. 8 g of NaOH is dissolved in 18 g of H_2O. Mole fraction of NaOH in solution and molality (in mol kg^{-1}) of the solution respectively are

(a) 0.167, 11.11 (b) 0.2, 22.20

(c) 0.2, 11.11 (d) 0.167, 22.20

(JEE Main 2019)

B81. The amount of sugar ($C_{12}H_{22}O_{11}$) required to prepare 22 of its 0.1 M aqueous solution is

(a) 68.4 g (b) 17.1 g

(c) 34.2 g (d) 136.8 g

(JEE Main 2019)

B82. A solution of sodium sulphate contains 92 g of Na^+ ions per kilogram of water. The molality of Na^+ ions in that solution in mol kg^{-1} is

(a) 16 (b) 8

(c) 4 (d) 12

(JEE Main 2019)

JEE (Advance) for IIT Entrance

B83. Given that the abundances of isotopes ^{54}Fe, ^{56}Fe and ^{57}Fe are 5%, 90% and 5% respectively, the atomic mass of Fe is

(a) 55.85 (b) 55.95

(c) 55.75 (d) 56.05 *(IIT-JEE 2009)*

Answers

B74. (d) **B75.** (b) **B76.** (b) **B77.** (a) **B78.** (a) **B79.** (d) **B80.** (a) **B81.** (a) **B82.** (c) **B83.** (b)

C MULTIPLE CHOICE QUESTIONS
with more than one correct answers

C1. Which of the following method/methods of expressing concentrations is/are independent of temperature ?

(a) Mole fraction (b) Molarity

(c) Normality (d) Molality

C2. A solution contains 25% water, 25% ethanol (C_2H_5OH) and 50% acetic acid (CH_3COOH) by mass. The mole fraction of

(a) Water = 0.502

(b) Ethanol = 0.302

(c) Acetic acid = 0.196

(d) Ethanol + acetic acid = 0.498

C3. 8 g of O_2 has the same number of oxygen atoms as

(a) 11 g CO_2 (b) 14 g CO

(c) 32 g SO_2 (d) 8 g O_3

C4. The mass of $\frac{1}{12}$ th of ^{12}C is same as that of

(a) $\frac{1}{28}$ th of N_2 (b) 1u

(c) $\frac{1}{8}$ th of O (d) $\frac{1}{12}$ th of He

C5. In $MgSO_4$ (at. mass : Mg = 24, S = 32, O = 16), the mass percentage of

(a) Mg = 80% (b) Mg = 20%

(c) S = 26.7% (d) S = 53.3%

Answers

C1. (a,d) **C2.** (a,d) **C3.** (a,b,d) **C4.** (a,b) **C5.** (b,c)

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C6. The following substances are present in different containers

(*i*) One gram atom of nitrogen

(*ii*) One mole of calcium

(*iii*) One atom of silver

(*iv*) One mole of oxygen molecules

(*v*) 10^{23} atoms of carbon and

(*vi*) One gram of iron.

The correct order of increasing masses (in grams) is/are :

(*a*) (*iii*) < (*vi*) < (*i*) < (*v*)

(*b*) (*iii*) < (*vi*) < (*iv*) < (*ii*)

(*c*) (*vi*) < (*v*) < (*i*) < (*iv*)

(*d*) (*iii*) < (*ii*) < (*v*) < (*iv*)

C7. Which of the following methods of expressing concentration varies with temperature?

(*a*) Molality (*b*) Weight per cent

(*c*) Normality (*d*) Molarity

C8. Which of the following units are not correct for the physical quantity ?

(*a*) Acceleration : ms^{-2} (*b*) Pressure : $kg\ m^{-2}s^{-2}$

(*c*) Power : Js (*d*) Frequency : s^{-1}

Answers

C6. (*b, c*) **C7.** (*c, d*) **C8.** (*b, c*)

D MULTIPLE CHOICE QUESTIONS

based on the given passage/comprehension

Passage-I

A mole is a collection of 6.022×10^{23} particles and the number 6.022×10^{23} is called Avogadro number. The mass of this number of atoms in an element is equal to its gram atomic mass and mass of this number of molecules in a compound is equal to its gram molecular mass. The volume occupied by this number of molecules of a gas at N.T.P is 22.4 L. When 6.022×10^{23} molecules of a substance are dissolved in 1 L of solution, the solution is known as 1 molar volume.

Answer the following questions :

D1. The mass of 10 molecules of naphthalene ($C_{10}H_8$) is

(*a*) 2.12×10^{-22} g (*b*) 2.12×10^{-21} g

(*c*) 2.12×10^{-23} g (*d*) 1280 g

D2. Suppose the chemists would have choosen 10^{20} as the number of particles in a mole, the mass of 1 mole of oxygen gas would be

(*a*) 5.32×10^{-43} g (*b*) 5.32×10^{-3} g

(*c*) 5.32×10^{-23} g (*d*) 5.32×10^{3} g

D3. One million atoms of silver (at. mass = 107.81) atoms weigh

(*a*) 1.79×10^{-16} g (*b*) 3.58×10^{-16} g

(*c*) 3.58×10^{6} g (*d*) 1.79×10^{16} g

Passage-II

The earlier method for determining the molecular weight of proteins was based on chemical analysis. The following composition of proteins were found :

Haemoglobin : 0.335% Fe

Cytochrome protein : 0.376% Fe

Peroxidase enzyme : 0.29% Se

Answer the following questions :

D4. If haemoglobin contains 4 atoms of iron, then approximate molecular mass of haemoglobin is (at. mass of Fe = 55.85)

(*a*) 16700 (*b*) 33400 (*c*) 66800 (*d*) 1670

D5. The mole % of Se in the enzyme peroxidase is (at. mass of Se = 78.96)

(*a*) 2.16×10^{-3} (*b*) 2.7×10^{5}

(*c*) 3.67×10^{-3} (*d*) 1.83×10^{-3}

D6. If the cytochrome protein contains one atom per molecule then the molecular mass of protein is

(*a*) 14850 u (*b*)29600 u

(*c*) 32960 u (*d*)12840 u

D7. How many atoms of Se are present in 1 μg of peroxidase enzyme assuming one molecule of enzyme contains 1 atom of Se (at. mass of Se = 78.96) ?

(*a*) 2.23×10^{19} (*b*) 4.52×10^{14}

(*c*) 3.82×10^{21} (*d*) 2.23×10^{6}

D8. How many moles of iron are present in 1 mg of haemoglobin (assuming a molecule of haemoglobin contains 4 Fe atoms)?

(*a*) 1.50×10^{-8} (*b*) 6.0×10^{-8}

(*c*) 3.0×10^{-8} (*d*) 1.875×10^{-9}

Answers

Passage I. **D1.** (*b*) **D2.** (*b*) **D3.** (*a*) **Passage II.** **D4.** (*c*) **D5.** (*c*) **D6.** (*a*) **D7.** (*b*) **D8.** (*b*)

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Passage III

Oleum or fuming sulphuric acid contains SO_3 dissolved in sulphuric acid and has the molecular formula $H_2S_2O_7$. It is formed by passing SO_3 in H_2SO_4. When water is added to oleum, SO_3 reacts with water to form H_2SO_4.

$$SO_3\,(g) + H_2O\,(l) \longrightarrow H_2SO_4\,(aq)$$

As a result, mass of H_2SO_4 increases. When 100 g sample of oleum is diluted with desired amount of water (in gram) then the total mass of pure H_2SO_4 obtained after dilution is known as percentage labelling of oleum.

% Labelling of oleum = Total mass of H_2SO_4 present in oleum after dilution

or = Mass of H_2SO_4 initially present + Mass of H_2SO_4 produced after dilution

From this, the percentage composition of H_2SO_4 and SO_3 (free) and SO_3 (combined) can be calculated.

Answer the following questions :

D9. The percentage of SO_3 in 109% H_2SO_4 is

(*a*) 9% (*b*) 36%

(*c*) 40% (*d*) 60%

D10. The percentage of free SO_3 and H_2SO_4 in 112% H_2SO_4 is

(*a*) 53.6, 46.4 (*b*) 12.0, 88.0

(*c*) 88.0, 12.0 (*d*) 26.8, 73.2

Answers

Passage III. D9. (*c*) **D10.** (*a*)

Assertion Reason Type Questions

The questions given below consist of an Assertion and the Reason. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

(*b*) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.

(*c*) If assertion is CORRECT, but reason is INCORRECT.

(*d*) If assertion is INCORRECT but reason is CORRECT.

(*e*) If both assertion and reason are INCORRECT.

1. Assertion : 22 carat gold is a compound.
Reason : A compound has fixed composition of the elements present in it.

2. Assertion : Both 32 g of SO_2 and 8 g of CH_4 contain same number of molecules.
Reason : Equal moles of two compounds contain same number of molecules.

3. Assertion : The standard unit for expressing the mass of atoms is a.m.u.
Reason : a.m.u. stands for mass of 1 atom of carbon.

4. Assertion : The sum of 154.2 + 6.1 + 23 is 183.
Reason : The result of addition is reported to the same number of decimal places as that of the term with least number of decimal places.

5. Assertion : 1 mol of O and 1 mol of O_2 contain equal number of particles.
Reason : 1 mol of molecules is always double than 1 mol of atoms in all diatomic molecules.

6. Assertion : Graphite is an element.
Reason : Element is the pure form of a substance containing same kind of atoms.

7. Assertion : Steam is a mixture.
Reason : In a compound, the composition of the elements must be fixed.

8. Assertion : Empirical and molecular formula of Na_2CO_3 is same.
Reason : Na_2CO_3 does not form hydrate.

9. Assertion : The empirical mass of ethene is half of its molecular mass.
Reason : The empirical formula represents the simplest whole number ratio of various atoms present in a compound.

10. Assertion : Significant figures for 0.200 is 3 whereas for 200 it is 1.
Reason : Zero at the end or right of a number are significant provided they are not on the right side of the decimal point.

Answers

1. (*d*) **2.** (*a*) **3.** (*c*) **4.** (*a*) **5.** (*c*) **6.** (*a*) **7.** (*d*) **8.** (*c*) **9.** (*a*) **10.** (*c*).

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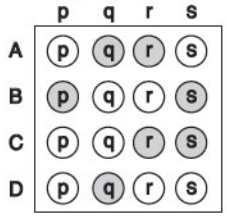
Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.



If the correct matches are A-*q*, A-*r*, B-*p*, B-*s*, C-*r*, C-*s* and D-*q*, then the correctly bubbled matrix will look like the following:

1. Match the physical quantity given in Column I with the symbol or definition in Column II

Column I	Column II
(A) Force	(*p*) J
(B) Energy	(*q*) s^{-1}
(C) Frequency	(*r*) kg m^2s^{-1}
(D) Work	(*s*) kg ms^{-2}

2. Match the term given in Column I with the description given in Column II.

Column I	Column II
(A) Molality	(*p*) independent of temperature
(B) Molarity	(*q*) mol L^{-1}
(C) Mole fraction	(*r*) g equiv L^{-1}
(D) Normality	(*s*) mol kg^{-1}

3. Match the following :

Column I	Column II
(A) 88 g of CO_2	(*p*) 0.25 mol
(B) 6.022×10^{23} molecules of H_2O	(*q*) 2 mol
(C) 5.6 litres of O_2 at STP	(*r*) 1 mol
(D) 96 g of O_2	(*s*) 6.022×10^{23} molecules
(E) 1 mol of any gas	(*t*) 3 mol

Answers

(1) : (A) – (*s*) (B) – (*p*), (*r*) (C) – (*q*) (D) – (*p*), (*s*)
(2) : (A) – (*p*), (*s*) (B) – (*q*) (C) – (*p*) (D) – (*r*)
(3) : (A) – (*q*) (B) – (*r*) (C) – (*p*) (D) – (*t*) (E) – (*s*)

Integer Type and Numerical Value Type Questions

Integer Type: The answer to each of the following question is a **single digit integer** ranging from 0 to 9.

1. 1.420 g of anhydrous $ZnSO_4$ was left in moist air. After a few days its weight was found to be 2.528 g. How many water molecules are present in its hydrated salt formula (molar mass of $ZnSO_4$ = 161.5)?

2. Moles of iron which can be made from Fe_2O_3 by the use of 294 g of carbon monoxide in the reaction :

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + CO_2 \text{ are :}$$

3. The ratio of molecular mass/empirical formula mass of a hydrocarbon having 92.4% C and vapour density of 39 is

4. 428 mL of 10 M HCl and 572 mL of 3 M HCl are mixed. The molarity of the resulting solution is

5. Silver (atomic mass = 108 g mol^{-1}) has a density of 10.5 cm^{-3}. The number of silver atoms on a surface of area $10^{-12}m^2$ can be expressed in scientific notation as $y \times 10^x$. The value of x is

(I.I.T. JEE 2010)

6. The value of n in the formula $Be_n\ Al_2\ Si_6\ O_{18}$ is

(I.I.T. 2010)

7. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is

(I.I.T. 2011)

8. 29.2% (w/w) HCl stock solution has a density of 1.25 g mL^{-1}. The molecular weight of HCl is 36.5 g mol^{-1}. The volume (mL) of stock solution required to prepare a 200 mL solution of 0.4 M HCl is

(I.I.T. J.E.E. 2012)

Answers

1. (7) **2.** (7) **3.** (6) **4.** (6) **5.** (7) **6.** (3) **7.** (5) **8.** (8)

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9. If the value of Avogadro number is 6.023×10^{23} and the value of Boltzmann constant is 1.380×10^{-23} JK^{-1}, then number of significant digits in the calculated value of the universal constant is *(JEE Advance 2014)*

Numerical Value Type: Give the correct numerical value (in decimal notation truncated/rounded off to the second decimal place.

10. To measure the quantity of $MnCl_2$ dissolved in an aqueous solution, it was completely converted to $KMnO_4$ using the reaction,

$$MnCl_2 + K_2S_2O_8 + H_2O \rightarrow KMnO_4 + H_2SO_4 + HCl$$

(equation not balanced)

Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 mg) was added in portions till the colour of the permanganate ion disappeared. The quantity of $MnCl_2$ (in mg) present in the initial solution is _____. (Atomic weights in g mol^{-1}: Mn = 55, Cl = 35.5) *(JEE Advanced 2018)*

Answers

9. (4) **10.** 126.00

NCERT Exemplar Problems

Multiple Choice Questions (Type-I)

1. Two students performed the same experiment separately and each one of them recorded two readings of mass which are given below. Correct reading of mass is 3.0 g. On the basis of given data mark the correct option out of the following statements.

Student	Readings	
	(*i*)	(*ii*)
A	3.01	2.99
B	3.05	2.95

(*a*) Results of both the students are neither accurate nor precise.

(*b*) Results of student A are both precise and accurate.

(*c*) Results of student B are neither precise nor accurate.

(*d*) Results of student B are both precise and accurate.

2. A measured temperature on Fahrenheit scale is 200°F. What will this reading be on Celsius scale ?

(*a*) 40°C (*b*) 94°C

(*c*) 93.3°C (*d*) 30°C

3. What will be the molarity of a solution, which contains 5.85g of NaCl(*s*) per 500 mL ?

(*a*) 4 mol L^{-1} (*b*) 20 mol L^{-1}

(*c*) 0.2 mol L^{-1} (*d*) 2 mol L^{-1}

Objective Questions

4. If 500 mL of a 5M solution is diluted to 1500 mL, what will be the molarity of the solution obtained ?

(*a*) 1.5 M (*b*) 1.66 M

(*c*) 0.017 M (*d*) 1.59 M

5. The number of atoms present in one mole of an element is equal to Avogadro number. Which of the following element contains the greatest number of atoms ?

(*a*) 4 g He (*b*) 46 g Na

(*c*) 0.40 g Ca (*d*) 12 g He

6. If the concentration of glucose ($C_6H_{12}O_6$) in blood is 0.9 g L^{-1}, what will be the molarity of glucose in blood ?

(*a*) 5 M (*b*) 50 M

(*c*) 0.005 M (*d*) 0.5 M

7. What will be the molality of the solution containing 18.25 g of HCl gas in 500 g of water ?

(*a*) 0.1 m (*b*) 1 M

(*c*) 0.5 m (*d*) 1 m

8. One mole of any substance contains 6.022×10^{23} atoms/molecules. Number of molecules of H_2SO_4 present in 100 mL of 0.02M H_2SO_4 solution is _____.

(*a*) 12.044×10^{20} molecules

(*b*) 6.022×10^{23} molecules

(*c*) 1×10^{23} molecules

(*d*) 12.044×10^{23} molecules

9. What is the mass percent of carbon in carbon dioxide ?

(*a*) 0.034 % (*b*) 27.27 %

(*c*) 3.4 % (*d*) 28.7%

Answers

1. (*b*) **2.** (*c*) **3.** (*c*) **4.** (*b*) **5.** (*d*) **6.** (*c*) **7.** (*d*) **8.** (*a*) **9.** (*b*)

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10. The empirical formula and molecular mass of a compound are CH_2O and 180 g respectively. What will be the molecular formula of the compound ?

(*a*) $C_9H_{18}O_9$ (*b*) CH_2O

(*c*) $C_6H_{12}O_6$ (*d*) $C_2H_4O_2$

11. If the density of a solution is 3.12 g mL^{-1}, the mass of 1.5 mL solution in significant figures is _____ .

(*a*) 4.7 g (*b*) 4680×10^{-3}g

(*c*) 4.680 g (*d*) 46.80 g.

12. Which of the following statements about a compound is incorrect ?

(*a*) A molecule of a compound has atoms of different elements.

(*b*) A compound cannot be separated into its constituent elements by physical methods of separation.

(*c*) A compound retains the physical properties of its constituent elements.

(*d*) The ratio of atoms of different elements in a compound is fixed.

13. Which of the following statements is correct about the reaction given below?

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(g)$$

(*a*) Total mass of iron and oxygen in reactants = total mass of iron and oxygen in product, therefore it follows law of conservation of mass.

(*b*) Total mass of reactants = total mass of product; therefore, law of multiple proportions is followed.

(*c*) Amount of Fe_2O_3 can be increased by taking any one of the reactants (iron or oxygen) in excess.

(*d*) Amount of Fe_2O_3 produced will decrease if the amount of any one of the reactants (iron or oxygen) is taken in excess.

14. Which of the following reactions is not correct according to the law of conservation of mass?

(*a*) $2Mg\,(s) + O_2\,(g) \longrightarrow 2MgO\,(s)$

(*b*) $C_3H_8\,(g) + O_2\,(g) \longrightarrow CO_2(g) + H_2O(g)$

(*c*) $P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}\,(s)$

(*d*) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

15. Which of the following statements indicates that law of multiple proportions is being followed?

(*a*) Sample of carbon dioxide taken from any source will always have carbon and oxygen in the ratio 1 : 2.

(*b*) Carbon forms two oxides namely CO_2 and CO, where masses of oxygen which combine with fixed mass of carbon are in the simple ratio 2 : 1.

(*c*) When magnesium burns in oxygen, the amount of magnesium taken for the reaction is equal to the amount of magnesium in magnesium oxide formed.

(*d*) At constant temperature and pressure 200 mL of hydrogen will combine with 100 mL oxygen to produce 200 mL of water vapour.

Answers

10. (*c*) **11.** (*a*) **12.** (*c*) **13.** (*a*) **14.** (*b*) **15.** (*b*)

Multiple Choice Questions (Type-II)

16. One mole of oxygen gas at STP is equal to

(*a*) 6.022×10^{23} molecules of oxygen

(*b*) 6.022×10^{23} atoms of oxygen

(*c*) 16 g of oxygen

(*d*) 32 g of oxygen

17. Sulphuric acid reacts with sodium hydroxide as follows :

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

When 1L of 0.1M sulphuric acid solution is allowed to react with 1L of 0.1M sodium hydroxide solution, the amount of sodium sulphate formed and its molarity in the solution obtained is

(*a*) 0.1 mol L^{-1} (*b*) 7.10 g

(*c*) 0.025 mol L^{-1} (*d*) 3.55 g

18. Which of the following pairs have the same number of atoms ?

(*a*) 16 g of $O_2(g)$ and 4 g of $H_2(g)$

(*b*) 16 g of O_2 and 44 g of CO_2

(*c*) 28 g of N_2 and 32 g of O_2

(*d*) 12 g of C(*s*) and 23 g of Na (*s*)

19. Which of the following solutions have the same concentration ?

(*a*) 20 g of NaOH in 200 mL of solution

(*b*) 0.5 mol of KCl in 200 mL of solution

(*c*) 40 g of NaOH in 100 mL of solution

(*d*) 20 g of KOH in 200 mL of solution

Answers

16. (*a, d*) **17.** (*b, c*) **18.** (*c, d*) **19.** (*a, b*)

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20. 16 g of oxygen has same number of molecules as in

(*a*) 16 g of CO (*b*) 28 g of N_2

(*c*) 14 g of N_2 (*d*) 1.0 g of H_2

21. Which of the following terms are unitless ?

(*a*) Molality (*b*) Molarity

(*c*) Mole fraction (*d*) Mass percentage

22. One of the statements of Dalton's atomic theory is given below :

"Compounds are formed when atoms of different elements combine in a fixed ratio."

Which of the following laws is not related to this statement ?

(*a*) Law of conservation of mass

(*b*) Law of definite proportions

(*c*) Law of multiple proportions

(*d*) Avogadro law

Answers

20. (*c*, *d*) **21.** (*c*, *d*) **22.** (*a*, *d*)

Matching Type Questions

23. Match the following :

(*i*) 88 g of CO_2	(*a*) 0.25 mol
(*ii*) 6.022×10^{23} molecules of H_2O	(*b*) 2 mol
(*iii*) 5.6 litres of O_2 at STP	(*c*) 1 mol
(*iv*) 96 g of O_2	(*d*) 6.022×10^{23} molecules
(*v*) 1 mol of any gas	(*e*) 3 mol

24. Match the following physical quantities with units :

Physical quantity	Unit
(*i*) Molarity	(*a*) $g\ mL^{-1}$
(*ii*) Mole fraction	(*b*) mol
(*iii*) Mole	(*c*) Pascal
(*iv*) Molality	(*d*) Unitless
(*v*) Pressure	(*e*) $mol\ L^{-1}$
(*vi*) Luminous intensity	(*f*) Candela
(*vii*) Density	(*g*) $mol\ kg^{-1}$
(*viii*) Mass	(*h*) Nm^{-1}
	(*i*) kg

Answers

23. (*i*) – (*b*); (*ii*) – (*c*); (*iii*) – (*a*); (*iv*) – (*e*); (*v*) – (*d*).

24. (*i*) – (*e*); (*ii*) – (*d*); (*iii*) – (*b*); (*iv*) – (*g*); (*v*) – (*c*); (*vi*) – (*f*); (*vii*) – (*a*); (*viii*) – (*i*).

Assertion and Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

25. Assertion (A) : The empirical mass of ethene is half of its molecular mass.

Reason (R) : The empirical formula represents the simplest whole number ratio of various atoms present in a compound.

(*a*) Both A and R are true and R is the correct explanation of A.

(*b*) A is true but R is false.

(*c*) A is false but R is true.

(*d*) Both A and R are false.

26. Assertion (A) : One atomic mass unit is defined as one twelfth of the mass of one carbon-12 atom.

Reason (R) : Carbon-12 isotope is the most abundant isotope of carbon and has been chosen as standard.

(*a*) Both A and R are true and R is the correct explanation of A.

(*b*) Both A and R are true but R is not the correct explanation of A.

(*c*) A is true but R is false.

(*d*) Both A and R are false.

Answers

25. (*a*) **26.** (*b*)

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27. Assertion (A) : Significant figures for 0.200 is 3 where as for 200 it is 1.

Reason (R) : Zero at the end or right of a number are significant provided they are not on the right side of the decimal point.

(*a*) Both A and R are true and R is the correct explanation of A.

(*b*) Both A and R are true but R is not a correct explanation of A.

(*c*) A is true but R is false.

(*d*) Both A and R are false.

28. Assertion (A) : Combustion of 16 g of methane gives 18 g of water.

Reason (R) : In the combustion of methane, water is one of the products.

(*a*) Both A and R are true but R is not the correct explanation of A.

(*b*) A is true but R is false.

(*c*) A is false but R is true.

(*d*) Both A and R are false.

Answers

27. (*c*) **28.** (*c*)

Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A4. (*b*) : Ratio of X and Y in compound A is 1:1
Ratio of X and Y in compound C is 1:3
Now, if in compound A, 28 parts by wt.of X combine with 16 parts by wt. of Y, then in compound C, 28 parts of X will combine with $16 \times 3 = 48$ parts of Y.
$\therefore$ 24 parts by wt. of Y will combine with 14 parts of X in compound C.

A5. (*d*) : In first oxide : Metal = 42.9 parts and
oxygen = 57.1 parts
Since the formula is MO.
$\therefore$ 42.9 parts of metal = 1 atom
57.1 parts of oxygen = 1 atom
In second oxide, metal = 27.3 parts and
oxygen = 72.7 parts
Now, 42.9 parts of metal = 1 atom

$$27.3 \text{ parts of metal} = \frac{1}{42.9} \times 27.3$$

$$= 0.636 \text{ atoms and}$$

57.1 parts of oxygen = 1 atom

$$72.7 \text{ parts of oxygen} = \frac{1}{57.1} \times 72.7$$

$$= 1.267 \text{ atoms}$$

Ratio of M : O = 0.636 : 1.267
or = 1 : 2
Formula = MO_2.

A6. (*c*) : 4.26 – (15.635/5.0)
4.26 – 3.1 (upto two signicicant figures)
= 1.2 (upto first decimal place after rounding off).

A7. (*d*) : Different weights are (*a*) 88g (*b*) 34.2g. (*c*) 40g (*d*) 27g. 27g (1.5 mol) of water weigh least.

A8. (*d*) : (*a*) $6.022 \times 10^{23} \times 3$ (*b*) $0.5 \times 6.022 \times 10^{23} \times 2$
(*c*) $0.1 \times 6.022 \times 10^{23} \times 3$ (*d*) $1 \times 6.022 \times 10^{23} \times 5$.

A11. (*a*) : No. of atoms of P_4 = $0.1 \times 6.02 \times 10^{23} \times 4$
= 2.4×10^{23} atoms.

A12. (*a*) : Moles of NH_3 = $\frac{8.5}{17} = 0.5$

No. of H atoms = $0.5 \times 6.022 \times 10^{23} \times 3$
= 9.03×10^{23} atoms.

A13. (*c*) : No. of molecules of O_3 in 22.4 L = 6.022×10^{23}
No. of molecules of O_3 in 11.2 L

$$= \frac{1}{2} \times 6.022 \times 10^{23}$$

No. of O atoms = $\frac{1}{2} \times 3 \times 6.022 \times 10^{23}$
= 9.03×10^{23}.

A14. (*c*) : Mass of 1 He atom = 4 a.m.u.

No. of He atoms = $\frac{104}{4} = 26$

A15. (*c*) : Moles of water = $\frac{0.018}{18} = 1 \times 10^{-3}$

Molecules of water = $6.022 \times 10^{23} \times 10^{-3}$
= 6.022×10^{20}

A16. (*c*) : No. of O atoms in 34.2 g of $C_{12}H_{22}O_{11}$.

$$= \frac{6.02 \times 10^{23} \times 34.2}{342} \times 11$$

$$= 6.62 \times 10^{23}$$

No. of O atoms in 90 g of H_2O

$$= \frac{6.02 \times 10^{23} \times 90}{18} \times 1$$

$$= 3.01 \times 10^{24}$$

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Total number of O atoms

$= 0.662 \times 10^{24} + 3.01 \times 10^{24}$

$= 3.67 \times 10^{24}$.

A21. (*c*) : 22400 mL of water contain molecules

$= 6.022 \times 10^{23}$

1 mL of water contains molecules

$= \frac{6.022 \times 10^{23}}{22400} = 2.69 \times 10^{19}$.

A22. (*b*) : $2\text{ g O} = \frac{2}{16} = \frac{1}{8}$ mol

$4\text{ g S} = \frac{4}{32} = \frac{1}{8}$ mol

These will contain same number of atoms.

A23. (*a*) : Caustic soda is NaOH

40 g of NaOH contain 6.02×10^{23} molecules

$= 6.02 \times 10^{23}$ atoms of H.

A24. (*b*) : $C + O_2 \longrightarrow CO_2$

12 g of C gives $CO_2 = 44$ g

0.6 g of C will give $CO_2 = \frac{44}{12} \times 0.6 = 2.2$ g

Moles of $CO_2 = \frac{2.2}{44} = 0.05$

No. of molecules $= 0.05 \times 6.02 \times 10^{23}$

$= 3.01 \times 10^{22}$

A25. (*a*) : 1 molecule of CH_4 contains electrons $= 6 + 4 = 10$

16 g of CH_4 contain 6.022×10^{23} molecules

$= 6.022 \times 10^{23} \times 10$ electrons

$\therefore$ 3.2 g of CH_4 contain $= \frac{6.022 \times 10^{23} \times 10 \times 3.2}{16}$

$= 2 \times 10 \times 6.022 \times 10^{22}$ electrons.

A26. (*d*) : Moles of $NH_3 = \frac{4.25}{17}$

No. of atoms $= \frac{4.25}{17} \times 6.02 \times 10^{23} \times 4$

$= 6.02 \times 10^{23}$.

A27. (*b*) : Fe present in 67200 u $= \frac{0.33}{100} \times 67200$

$= 221.8$ u

No. of iron atoms present in 67200 u $= \frac{221.8}{56} = 4$

A28. (*d*) : Mass of 1 mol of electrons

$= 9.108 \times 10^{-31} \times 6.02 \times 10^{23}$ kg

1 kg of electrons $= \frac{1}{9.108 \times 6.02} \times 10^{8}$ mol.

A29. (*d*) : Suppose 1 molecule of alkaloid contains x atoms of N

$\therefore$ % of N $= \frac{14 \times x}{162} \times 100 = 17.28$

$\therefore$ $x = \frac{17.28 \times 162}{14 \times 100} = 2$

No. of N atoms in alkaloid = 2

A30. (*a*) : No. of atoms of Fe $= \frac{558.6}{55.86} \times 6.02 \times 10^{23}$

$= 10 \times 6.02 \times 10^{23}$

No. of atoms in 60 g of C $= \frac{60}{12} \times 6.02 \times 10^{23}$

$= 5 \times 6.02 \times 10^{23}$

$\therefore$ No. of atoms in 558.6 g of Fe = twice the no. of atoms in 60 g of C.

A31. (*c*) : Molecular formula of sucrose = $C_{12}H_{22}O_{11}$

Empirical formula = $C_{12}H_{22}O_{11}$.

A32. (*c*) : $Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$

1 mol of Ca_3P_2 gives 2 moles of PH_3.

A33. (*b*) : Out of 1 mole of water, number of moles of D_2O

$= \frac{x \times 1}{100} = 0.01\,x$

Number of moles of $D_2O \times$ mass of D_2O + Number of moles of $H_2O \times$ mass of $H_2O = 19$

$0.01x \times 20 + (1 - 0.01x) \times 18 = 19$

$0.01x \times 20 + 18 - 0.01x \times 18 = 19$

$0.2x - 0.18x = 1$

$0.02x = 1$

$x = 1/0.02 = 50$

A34. (*d*) : Let '*a*' atoms of sulphur be present in x g of the compound.

8% of weight of compound = weight of sulphur in compound

$\frac{8}{100}x = 32 \times a$

$x = \frac{3200}{8}a = 400\,a$

The minimum molecular weight is the one in which $a = 1$ (*i.e.* 1 atom of sulphur is present).

Hence, minimum molecular weight = 400

A35. (*a*) : Normality of oxalic acid $= \frac{6.3}{63} \times \frac{1000}{250} = 0.4$ N

$N_1V_1 = N_2V_2$

$0.4 \times 10 = 0.1 \times V_2$

$V_2 = \frac{0.4 \times 10}{0.1} = 40$ mL.

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A36. (*a*) : Mixture X contains 0.02 mol Br^- and 0.02 mol SO_4^{2-} in 2 L.

$\therefore$ 1 L of X will contain 0.01 mol Br^- and 0.01 mol SO_4^{2-}

With excess of $AgNO_3$, 0.01 mol of AgBr *i.e.*, Y is formed.

With excess of $BaCl_2$, 0.01 mol of $BaSO_4$ *i.e.*, Z is formed.

A37. (*b*) : $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

1 L of N_2 reacts with 3 L of H_2 to form 2 L of NH_3.

Thus, H_2 is limiting reagent.

10 L of N_2 will react with 30 L of H_2 to form 20 L of NH_3.

Since actual yield is 50% of the expected value,

NH_3 formed = 10 L

N_2 reacted = 5 L

N_2 Unreacted = 30 – 5 = 25 L

H_2 reacted = 15 L

H_2 Unreacted = 30 – 15 = 15 L

$\therefore$ Mixture will contain 10 L NH_3, 25 L N_2, 15 L H_2.

A38. (*d*): Equal volumes contain equal no. of moles

$\therefore$ Molar ratio = 1 : 1

Ratio by weight = 4 : 16 = 1 : 4

$\therefore$ CH_4 present by weight

$$= \frac{4}{5} \times 100 = 80\%$$

A39. (*d*): $2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$

4 × 27 kg of Al consumes C of anode

= 3× 12 = 36 kg

Production of 270 kg of Al consumes C of anode

$$= \frac{36}{4 \times 27} \times 270 = 90 \text{ kg}$$

A40. (*d*): Molecular mass of $Na_2SO_4 = 2 \times 23 + 32 + 4 \times 16$

= 142

A crystalline salt on becoming anhydrous loses 55.9% by mass.

44.1 g of anhydrous salt contain H_2O = 55.9

142 g of anhydrous salt contain H_2O

$$= \frac{55.9}{44.1} \times 142 = 180 \text{ g}$$

No. of water molecules = $\frac{180}{18}$ = 10 molecules

A41. (*a*) : $N_2 + 3H_2 \longrightarrow 2NH_3$

1 mol of N_2 (28g) combine with 3 mol (6g) of H_2

$\therefore$ 3 kg of N_2 will react with $\frac{28}{3} \times 3$ = 14 kg of N_2

H_2 is the limiting reagent.

6g of H_2 produce NH_3 = 34g

3.0 kg of H_2 will produce $NH_3 = \frac{34}{6} \times 3 = 17$ kg

A42. (*a*):

Element	Percentage	Atomic ratio	Simplest ratio	Whole no. ratio
P	43.6%	$\frac{43.6}{31} = 1.41$	$\frac{1.41}{1.41} = 1$	2
O	56.4%	$\frac{56.4}{16} = 3.52$	$\frac{3.52}{1.41} = 2.5$	5

Formula = P_2O_5

A43. (*c*): 38 g of HCl is present in 100 g of solution

$$\text{Vol. of solution} = \frac{100}{1.19}$$

$$\text{Molarity} = \frac{\frac{38}{36.5} \times 1000}{\frac{100}{1.19}}$$

= 12.38 M

A44. (*b*): $M_1V_1 + M_2V_2 = M(V_1 + V_2)$

$0.5 \times 800 + 1 \times 200 = M\,(800 + 200)$

$$M = \frac{400 + 200}{1000} = 0.6\,M$$

A45. (*b*): Final volume = 2 L + 4 L = 6 L

$$\text{Molarity} = \frac{6 \times 2}{6} = 2 \text{ M}$$

A46. (*d*):

$$M_1V_1 = M_2V_2$$

$$10.50 \times V_1 = 0.25 \times 1.0$$

$$V_1 = \frac{0.25 \times 1.0}{10.50}$$

$$= 0.0238 \text{ L} = 23.8 \text{ mL}$$

A47. (*c*) :

$$\text{Molarity} = \frac{\text{Moles}}{\text{Vol (in mL)}} \times 1000$$

$$0.50 = \frac{\text{Moles}}{250} \times 1000$$

$$\text{Moles of NaCl} = \frac{0.50 \times 250}{1000}$$

= 0.125 mol.

A48. (*d*) :

$$C_xH_y(g) + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2(g) + \frac{y}{2}H_2O(l)$$

1 mL	$\left(x + \frac{y}{4}\right)$ mL	x mL	negligible
6 mL	$6\left(x + \frac{y}{4}\right)$ mL	$6x$ mL	

Equating theoretical and experimental value of CO_2

$6x = 12$ or $x = 2$

Theoretical value of contraction after explosion and cooling for 1mL of hydrocarbon

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$$1+\left(x+\frac{y}{4}\right)-x=1+\frac{y}{4}$$

For 6 mL of hydrocarbon contraction on explosion and cooling = 9 mL

For 1 mL of hydrocarbon contraction on explosion and cooling $=\frac{9}{6}=1.5$ mL

Equating

$$1+\frac{y}{4}=1.5 \quad \text{or} \quad \frac{y}{4}=0.5 \quad \text{or} \quad y=2$$

$\therefore$ Formula of hydrocarbon = C_2H_2

B. *mcq from competitive examinations*

B1. (*b*) : $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$

22.4 L $\quad$ 5×22.4 L

at N.T.P. $\quad$ at N.T.P.

22.4 L of C_3H_8 at N.T.P. require $O_2 = 5 \times 22.4$ L

1 L of C_3H_8 at N.T.P. will require O_2

$$=\frac{5\times22.4}{22.4}\text{ L at N.T.P.}$$

$$= 5 \text{ L}$$

B2. (*c*) : $PbO + 2HCl \longrightarrow PbCl_2 + H_2O$

Molar mass of PbO = 207 + 16 = 223 g mol^{-1}

$$\text{Moles of PbO} = \frac{6.5}{223} = 0.029 \text{ mol}$$

$$\text{Moles of HCl} = \frac{3.2}{36.5} = 0.088 \text{ mol}$$

1 mol of PbO reacts with 2 mol of HCl

$\therefore$ PbO is a limiting reagent

0.029 mol of PbO will produce $PbCl_2$ = 0.029 mol.

B3. (*b*) : Mass of 1 molecule of water $=\frac{18}{6.022\times10^{23}}$ g

$$\text{Volume} = \frac{18 \text{ g}}{6.022\times10^{23}\times1 \text{ g/cm}^3} = 3.0 \times 10^{-23} \text{ cm}^3$$

B4. (*b*) : Molality and mole fraction are independent of temperature.

B5. (*b*) : $2H_2 + O_2 \longrightarrow 2H_2O$

10 g = 5 mol $\quad$ 64 g = 2 mol

Limiting reagent is O_2

1 mole of O_2 gives 2 moles of H_2O

$\therefore$ 2 moles of O_2 will give 4 moles of H_2O.

B6. (*c*) $\quad$ Normality = n × Molarity

For acids, $\quad n$ = Basicity

$\therefore$ For H_2SO_4, $\quad n = 2$

$$0.02 \text{ N} = 2 \times \text{Molarity}$$

or $\quad$ Molarity of 0.02 N H_2SO_4

$$=\frac{0.02}{2}=0.01\text{M}$$

0.01 M solution of H_2SO_4 contains 0.01 moles of H_2SO_4 in 1000 mL solution.

$\therefore$ Number of moles in 100 mL solution

$$=\frac{0.01}{1000}\times100$$

$$= 0.001 \text{ moles}$$

Number of molecules in 0.001 moles

$$= 6.022 \times 10^{23} \times 0.001$$

$$= 6.022 \times 10^{20} \text{ molecules}$$

B7. (*b*) $\quad 4Al + 3O_2 \longrightarrow 2Al_2O_3$

$4 \times 27 = 54$ g $\quad$ 3 mol

Amount of Al that combines with 3 moles of O_2

$$= 54 \text{ g}$$

$\therefore$ Amount of Al that combines with 1.5 moles of O_2 = 27 g

B8. (*d*) $\quad A + 2B \longrightarrow C$

1 Mol $\quad$ 2 Mol $\quad$ 1 mol

8 moles of B require 4 moles of A. Therefore, limiting reagent is B.

2 moles of B give 1 mole of C

$\therefore$ 8 moles of B give $=\frac{1}{2}\times8=4$ moles of C.

B9. (*b*) $\quad$ 1 kg of sea water = 10^6 mg sea water

10^6 mg sea water has 6 mg dissolved O_2

The concentration of $O_2 = \frac{6}{10^6}\times10^6$ ppm

$$= 6 \text{ ppm}$$

B10. (*c*) $\quad \text{Molarity} = \frac{25.3/106}{250}\times1000$

$$= 0.955 \text{ M}$$

$$Na_2CO_3 \longrightarrow 2Na^+ + CO_3^{2-}$$

$\therefore$ $\quad [Na^+] = 2 \times 0.955 = 1.910$ M

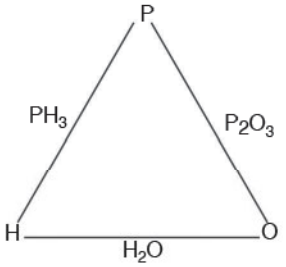
$$[CO_3^{2-}] = 0.955 \text{ M}$$

B11. (*c*) $\quad$ No. of atoms in 0.1 mol

$$= 6.022 \times 10^{23} \times 0.1 \times 3$$

$$= 1.806 \times 10^{23}$$

B12. (*a*)



Ratio of number of hydrogen and oxygen combining with one P is

3 : 1.5 *i.e.*, 2 : 1

It is same as in water (2 : 1)

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B13. (*a*) $N_2 + 3H_2 \longrightarrow 2NH_3$
28 2×3 34
1 mole of N_2 (28 g) combine with 3 moles of H_2 (6 g)
$\therefore$ 3 kg of H_2 can react with $\frac{28}{6} \times 3 = 14$ kg of N_2
H_2 is limiting reagent.
Moles of NH_3 formed = $\frac{34}{6} \times 3 = 17$ kg.

B14. (*b*) Moles of solute = 1 m
Moles of solvent = $\frac{1000}{18} = 55.56$
Mole fraction of solute = $\frac{1}{1+55.56} = \mathbf{0.0177}$.

B15. (*b*) $CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$
1 mol 1 mol
100g 22.4L
100g of $CaCO_3$ liberate CO_2 = 22.4L
10g of $CaCO_3$ will liberate $CO_2 = \frac{22.4}{100} \times 10 = 2.24$L

B16. (*c*) (*a*) 0.2 mol of H_2 gas = $0.2 \times 2 = 0.4$ g
(*b*) 6.023×10^{23} molecules of N_2 = 28g
6.023×10^{22} molecules of N_2
$= \frac{28}{6.023 \times 10^{23}} \times 6.023 \times 10^{22} = 2.8$g
(*c*) Weight of silver = 0. 1g
(*d*) 0.1 mol of O_2 gas = $0.1 \times 32 = 3.2$ g
(*e*) Weight of water = 1g
$\therefore$ 0.1 g of silver (*c*) is the lightest.

B17. (*a*) 22.4 L of H_2 at S.T.P. = 1 mol
11.2 L of Cl_2 at S.T.P. = 0.5 mol
So, Cl_2 is limiting reagent.
$H_2 + Cl_2 \longrightarrow 2HCl$
1 mol of Cl_2 reacts with 1 mol of H_2 to give 2 mol of HCl
$\therefore$ 0.5 mol of Cl_2 will react with 0.5 mol of Cl_2 to give 1 mol of HCl.

B18. (*a*) Moles of Mg = $\frac{1}{24} = 0.0417$ mol
Moles of O_2 = $\frac{0.56}{32} = 0.0175$ mol
$Mg + \frac{1}{2}O_2 \longrightarrow MgO$
1 mol 0.5 mol 1 mol
O_2 is limiting reagent
0.5 mol of O_2 react with Mg to form 1 mol of MgO
0.0175 mol of O_2 react with Mg = $\frac{1 \times 0.0175}{0.5}$
$= 0.035$
Moles of Mg left unreacted = $0.0417 - 0.035$
$= 6.7 \times 10^{-3}$ mol
Amount of Mg left unreacted = $6.7 \times 10^{-3} \times 24$
$= 0.1608$ g

B19. (*a*) $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$
According to equation, 1 mol of $CaCO_3$ reacts with 2 mol of HCl
Moles of HCl = $\frac{20}{1000} \times 1.0 = 0.02$ mol
Moles of $CaCO_3$ required = $\frac{0.02}{2} = 0.01$ mol
Mass of $CaCO_3$ required = $0.01 \times 100 = 1$ g

B20. (*e*) (*a*) 16 g $O_2 = \frac{16}{32} = 0.5$ mol = $0.5 \times N_A$ molecules
(*b*) 16 g $NO_2 = \frac{16}{46} = 0.35$ mol = $0.35 \times N_A$ molecules
(*c*) 4 g $N_2 = \frac{4}{28} = 0.14$ mol = $0.14 \times N_A$ molecules
(*d*) 2 g $H_2 = \frac{2}{2} = 1$ mol = N_A molecules
(*e*) 32 g $N_2 = \frac{32}{28} = 1.14$ mol = $1.14 \times N_A$ molecules
$\therefore$ (*e*) 32 of N_2 has maximum number of molecules

B21. (*d*) Let masses of H_2 and O_2 be x and $4x$ g
Moles of $H_2 = \frac{x}{2}$
Mole of $O_2 = \frac{4x}{32}$
Mole ratio = $\frac{x/2}{4x/32} = \frac{4}{1}$

B22. (*d*) Mass of 1 mol (6.022×10^{23} atoms of carbon = 12 g)
If Avogadro number is changed to 6.022×10^{20} atoms, then mass of 1 mol of carbon
$= \frac{12 \times 6.022 \times 10^{20}}{6.022 \times 10^{23}}$
$= 12 \times 10^{-3}$ g

B23. (*b*) (*a*) 18 g of water = $\frac{18}{18} = 1$ mol
$= N_A$ molecules
(*b*) 18 mol of water = $18 \times N_A$ molecules
(*c*) 18 molecules of water
(*d*) 1.8 g of water = $\frac{1.8}{18} = 0.1 \times N_A$ molecules
$\therefore$ 18 mol of water has maximum number of water molecules.

B24. (*b*) $MgCO_3$ (s) $\longrightarrow$ MgO (s) + CO_2 (g)
1 mol 1 mol
84 g 40 g
40 g of MgO are produced from $MgCO_3$ = 84 g
8 g of MgO are produced from $MgCO_3 = \frac{84}{40} \times 8$
$= 16.8$ g

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$$\% \text{ Purity of } MgCO_3 = \frac{16.8}{20} \times 100$$
$$= 84\ \%$$

B25. (*b*) 1 m aqueous solution means 1 mol of solute is present in 1000 g of water

$\therefore$ Moles of solute = 1 mole

$$\text{Moles of water} = \frac{1000}{18} = 55.55 \text{ mol}$$

$$\text{Mole fraction of solute} = \frac{1}{1+55.55} = 0.0177$$

B26. (*a*) 16.9 % $AgNO_3$ solution means that 16.9 g of $AgNO_3$ is present in 100 mL of solution.

$$50 \text{ mL of solution contains } AgNO_3 = \frac{16.9}{100} \times 50$$
$$= 8.45 \text{ g}$$

or $$\frac{8.45}{170} = 0.049 \text{ mol}$$

5.8 % NaCl solution means that 5.8 g of NaCl is present in 100 mL of solution.

$$50 \text{ mL of solution contains NaCl} = \frac{5.8}{100} \times 50 = 2.9 \text{ g}$$

or $$\frac{2.9}{58.5} = 0.049 \text{ mol}$$

$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$

1 mol of $AgNO_3$ combines with 1 mol of NaCl to give 1 mol of AgCl

0.049 mol of $AgNO_3$ combines with 0.049 mol of NaCl to give AgCl

$= 0.049$ mol

$= 0.049 \times 143.5$

$= 7$ g

B27. (*a*) : Let atomic weight of element X is x and that of element Y is y.

For XY_2

0.1 mol of XY_2 = 10 g

$$1.0 \text{ mol of } XY_2 = \frac{10}{0.1} \times 1.0 = 100 \text{ g}$$

or $x + 2y = 100$ g mol^{-1} .....(*i*)

For X_3Y_2

0.05 mol of X_3Y_2 = 9 g

$$1 \text{ mol } X_3Y_2 = \frac{9}{0.05} = 180 \text{ g}$$

or $3x + 2y = 180$ g mol^{-1} .....(*ii*)

Subtracting eq. (*i*) from eq. (*ii*)

$2x = 80$ g mol^{-1} or $x = 40$ g mol^{-1}

and $40 + 2y = 100$

$$\text{or } y = \frac{100-40}{2} = 30 \text{ g mol}^{-1}$$

B28. (*b*) : Molarity depends upon temperature.

B29. (*a*) : 18 mL of water has maximum number of molecules.

(*a*) : 18 mL of water = 18 × 1 g/mL = 18 g

$$\text{Molecules of water} = \frac{18}{18} \times N_A = N_A$$

(*b*) 0.18 g of water

$$\text{Molecules of water} = \frac{0.18}{18} \times N_A = 0.01 \times N_A$$

(*c*) $$\text{Moles of water} = \frac{0.00224 \text{ L}}{22.4} = 0.0001$$

Molecules of water = $0.0001 \times N_A = 0.0001 \times N_A$

(*d*) 10^{-3} mol of water

Molecules of water = $10^{-3} \times N_A = 0.001\ N_A$

B30. (*a*) : If atomic mass unit on the scale of $\frac{1}{6}$ of C – 12 is 2 a.m.u. on the scale of $\frac{1}{12}$ of C–12, the mass of one mole of substance will become half of the normal value.

B31. (*c*) : For each mole of Al reacted 1.5 mole of H_2 (g) (or 33.6 L at STP) is formed and for each mole of HCl consumed 0.5 mole of H_2(g) (or 11.2 L at STP) is formed.

B32. (*b*) :
$$\text{Moles of oxygen} = \frac{80}{16} = 5 \text{ mol}$$
No. of atoms of oxygen $= 5 \times 6.022 \times 10^{23}$

$$\text{Moles of hydrogen in 5g} = \frac{5}{1} = 5 \text{ mol}$$

No. of atoms of hydrogen = $5 \times 6.022 \times 10^{23}$

B34. (*a*) :
$$N_1V_1 + N_2V_2 = NV$$
where $V_1 + V_2 = 1\text{L}$
or $V_2 = (1 - V_1)\text{L}$
$10 \times V_1 + 4\,(1-V_1) = 1 \times 7$
$10V_1 + 4 - 4V_1 = 7$
$6V_1 = 3$
$$V_1 = \frac{3}{6} = 0.5\text{L}$$
$V_2 = 1 - 0.5 = 0.5$ L

B35. (*b*) : 98% H_2SO_4 means 98 g H_2SO_4 is present in 100 g of solution.

Volume of 100 g solution

$$= \frac{100}{1.8} = 55.55 \text{ mL}$$

$$\text{Molarity} = \frac{\text{Moles of } H_2SO_4 \times 1000}{\text{Volume of solution}}$$
$$= \frac{98}{98 \times 55.55} \times 1000 = 18\text{M}$$

B36. (*a*) :
$$N_1V_1 + N_2V_2 = NV$$
where $V_1 + V_2 = 1\text{L} = 1000$ mL
or $V_2 = (1 - V_1)\text{L}$
$10 \times 20 + 36 \times 10 = N \times 1000$
$200 + 360 = 1000\ N$
$$\text{or } N = \frac{560}{1000} = 0.56\text{N}$$

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B37. (*b*) : $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$

Moles of $Ca(OH)_2$ present in 50 mL of 0.5 M solution

$$= \frac{0.5}{1000} \times 50 = 2.5 \times 10^{-2} \text{ mol}$$

Moles of $CaCO_3$ formed = 2.5×10^{-2} mol

$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$

Moles of HCl required

$= 2 \times 2.5 \times 10^{-2}$ mol

$= 5.0 \times 10^{-2}$ mol

Volume of 0.1 N HCl required

$$= \frac{0.1}{1000} \times x = 5.0 \times 10^{-2}$$

$$x = \frac{5.0 \times 10^{-2} \times 1000}{0.1} = 500 \text{ mL}$$

B38. (*b*) Time taken to distribute 10^{20} grains

= 1 second

Time taken to distribute 6.022×10^{23} grains

$$= \frac{1}{10^{20}} \times 6.022 \times 10^{23} \text{ seconds}$$

$$= \frac{6.022 \times 10^{23}}{10^{20} \times 60 \times 60} \text{ hours}$$

= 1.673 hours

B39. (*b*) Let atomic mass of metal = x, then

$$\% \text{ of oxygen in } M_2O = \frac{16}{2x + 16} \times 100 = 36.4$$

or $1600 = 72.8x + 582.4$

$$x = \frac{1600 - 582.4}{72.8} = 13.978$$

Now, in second oxide, oxygen and metal are 53.4% and 46.6% respectively.

∴ Atomic ratio = M : O

$$\frac{46.6}{13.978} : \frac{53.4}{16}$$

3.3 : 3.3

or 1 : 1

∴ Formula of metal oxide = MO

B40. (*a*) I. Mass of 1 atom of oxygen $= \frac{16}{6.022 \times 10^{23}}$

$= 2.66 \times 10^{-23}$ g.

II. Mass of 1 atom of nitrogen $= \frac{14}{6.022 \times 10^{23}}$

$= 2.32 \times 10^{-23}$ g.

III. Mass of 1×10^{-10} mol of oxygen = 16×10^{-10} g

IV. Mass of 1×10^{-10} mol of copper = 63×10^{-10} g

∴ Order of increasing atomic mass :

II < I < III < IV.

B41. (*c*) $C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$

$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

Moles of mixture, $n = \frac{pV}{RT}$

$$= \frac{1 \text{ atm} \times 41 \text{ L}}{(0.082 \text{ L atm K}^{-1}\text{mol}^{-1}) \times 500\text{K}}$$

= 1 mol

Let moles of $C_2H_6 = x$, moles of $C_2H_4 = 1 - x$

Oxygen required

$\frac{7}{2}x + (1 - x)3 = \frac{10}{3}$

$21x + 18 - 18x = 20$

$3x = 2$ or $x = 0.67$ mol

Moles of ethane = 0.67,

Moles of ethene = $1 - 0.67 = 0.33$

Mole fraction of ethane = $\frac{0.67}{1} = 0.67$,

Mole fraction of ethene = $\frac{0.33}{1} = 0.33$

B42. (*b*) $NaCl + CaCl_2 \xrightarrow{Na_2CO_3} CaCO_3$

Let wt. of $CaCl_2$ in mixture = x

and wt. of NaCl in mixture = $4.44 - x$

$CaCO_3 \longrightarrow CaO + CO_2$

Moles of Ca in $CaCl_2$ = Moles of Ca in $CaCO_3$

Moles of Ca in $CaCO_3$ = Moles of Ca in CaO

$$\frac{x}{111} = \frac{0.56}{56}$$

$$\therefore \quad x = \frac{0.56}{56} \times 111 = 1.11 \text{ g}$$

Wt. of NaCl in mixture = $4.44 - 1.11 = 3.33$ g

$$\% \text{ of NaCl} = \frac{3.33}{4.44} \times 100 = 75\%$$

B43. (*a*) Equivalents of HCl $= \frac{0.2 \times 50}{1000} = 10 \times 10^{-3}$

Equivalents of NaOH $= \frac{0.1 \times 50}{1000} = 5.0 \times 10^{-3}$

5.0×10^{-3} equivalents of NaOH will neutralise 5.0×10^{-3} equivalents of HCl

Equivalent of HCl left = $(10 - 5) \times 10^{-3} = 5 \times 10^{-3}$

Volume of solution = 50 + 50 = 100 cm^3

$$\text{Normality} = \frac{5 \times 10^{-3}}{100} \times 1000 = 0.05 \text{ N}$$

100 cm^3 of 0.05 N HCl is titrated against 0.5 N KOH.

$$\underbrace{N_1 \times V_1}_{HCl} = \underbrace{N_2 \times V_2}_{KOH}$$

$0.05 \times 100 = 0.5 \times V_2$

$$\therefore \quad V_2 = \frac{0.05 \times 100}{0.5} = \mathbf{10\ cm^3}.$$

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B44. (*b*) $MCO_3 \xrightarrow{\Delta} MO + CO_2$

1 mol 22400 cc

2g 448 cc

448 cc of CO_2 is evolved from MCO_3 = 2g

22400 cc of CO_2 will be evolved from

$$MCO_3 = \frac{2}{448} \times 22400$$

$$= 100 \text{ g}$$

$\therefore$ 1 mol of MCO_3 = 100 g

or Molecular mass of MCO_3 = 100 g mol^{-1}

If M is the atomic mass of metal,

$$M + 12 + 3 \times 16 = 100$$

$$\therefore \quad M = 100 - 12 - 48 = 40$$

$$\text{Equivalent wt.} = \frac{\text{Atomic mass}}{\text{Valency}} = \frac{40}{2} = 20$$

B45. (*c*) Mass of water = 18 mL × 1g mL^{-1} = 18 g

or = 1 mol

No. of molecules in 1 mol of water

$$= 6.02 \times 10^{23}$$

No. of electrons in 1 molecule of water

$$= 2 + 8 = 10$$

$\therefore$ No. of electrons in 1 mol of water

$$= 6.02 \times 10^{23} \times 10$$

$$= 6.02 \times 10^{24}$$

B46. (*a*) Let volume of solution A = x L

Volume of solution B = $(2 - x)$ L

$$M_1V_1 + M_2V_2 = M(V_1 + V_2)$$

$$0.5 \times x + 0.1\,(2 - x) = 0.2\,(2)$$

$$0.5x + 0.2 - 0.1x = 0.4$$

$$0.4x = 0.2$$

$$x = \frac{0.2}{0.4} = 0.5\text{L}$$

Vol. of A = 0.5 L, Vol. of B = 2.0 − 0.5 = 1.5 L

B47. (*d*) Moles of water in a drop of water = $\frac{0.018}{18} = 1 \times 10^{-3}$

1 mole of water = 6.022×10^{23} molecules

1×10^{-3} mol of water = $6.022 \times 10^{23} \times 1 \times 10^{-3}$

$= 6.022 \times 10^{20}$ molecules.

B48. (*c*) $\text{Molarity} = \frac{\text{Moles of } HNO_3}{\text{Volume}} \times 1000$

$$\text{or Moles of } HNO_3 = \frac{\text{Molarity} \times \text{Volume}}{1000}$$

$$= \frac{2.0 \times 250}{1000} = 0.5$$

$$\text{Mass of } HNO_3 = 0.5 \times 63 = 31.5 \text{ g.}$$

$$\text{Mass of 70\% } HNO_3 = \frac{31.5 \times 100}{70} = 45.0\text{g}$$

B49. (*b*) $M_1V_1 + M_2V_2 = M_{mix}(V_1 + V_2)$

$$0.5 \times 750 + 2 \times 250 = M_{mix}(1000)$$

$$M_{mix} = \frac{0.5 \times 750 + 2 \times 250}{1000}$$

$$= \frac{375 + 500}{1000} = 0.875 \text{ M}$$

B50. (*a*) Moles of CO_2 produced = $\frac{3.08}{44} = 0.07$

Moles of H_2O produced = $\frac{0.72}{18} = 0.04$

Combustion of hydrocarbon C_xH_y may be represented as :

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \longrightarrow x\,CO_2 + \frac{y}{2} H_2O$$

$$x = 0.07, \ \frac{y}{2} = 0.04$$

$$\therefore \quad y = 0.08$$

$$\frac{x}{y} = \frac{0.07}{0.08} = \frac{7}{8}$$

$\therefore$ Empirical formula of hydrocarbon C_7H_8.

B51. (*a*) $BaO + 2HCl \longrightarrow BaCl_2 + H_2O$

$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$

The reaction shows that 2 moles of mixture of BaO and CaO require 4 moles of HCl to react completely.

Moles of HCl in 100 cm^3 = $\frac{2.5 \times 100}{1000}$ = 0.25 mol

4 moles of HCl react with 2 moles of mixture

0.25 mol of HCl reacts with mixture = $\frac{2 \times 0.25}{4}$

= 0.125 mol

Let mass of CaO be x g so that mass of BaO

$$= (10 - x) \text{ g}$$

$$\frac{x}{56} + \frac{10 - x}{153} = 0.125$$

$$153x + 560 - 56x = 0.125 \times 56 \times 153 = 1071$$

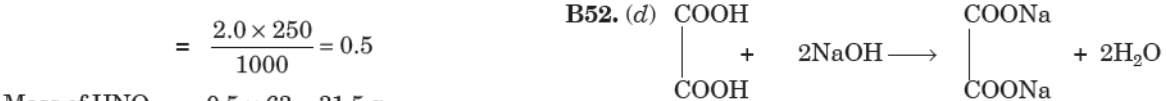
or $$97x = 1071 - 560 = 511$$

$$\therefore \quad x = \frac{511}{97} = 5.268$$

$$\therefore \quad \%\text{ CaO} = \frac{5.268}{10} \times 100$$

$$= 52.68\%$$

B52. (*d*)



Moles of 0.064 g of NaOH = $\frac{0.064}{40} = 0.0016$

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Since 2 moles of NaOH react with 1 mol of oxalic acid,

Moles of oxalic acid = $\frac{0.0016}{2} = 8 \times 10^{-4}$

Volume of solution = 25 mL

Molarity of oxalic acid solution = $\frac{8\times10^{-4}}{25} \times 1000$

$= 0.032$ M

B53. (*c*) 143.5 g of AgCl contain Ag = 108 g

Amount of Ag in 7.20 g of AgCl = $\frac{108}{143.5} \times 7.20$

$= 5.42$ g

% of Ag = $\frac{5.42}{5.82} \times 100 = 93.1\%$

B54. (*b*) $M_1V_1 + M_2V_2 \equiv M_3V_3$

$3.0 \times 25 + 4.0 \times 75 \equiv M_3 \times (25 + 75)$

$\therefore \quad 75 + 300 = M_3 \times 100$

$\therefore \quad M_3 = \frac{375}{100} = 3.75$ M

B55. (*c*) Ratio of masses of O_2 and N_2 =1 : 4

$\therefore$ Ratio of moles of O_2 and N_2 = $\frac{1}{32} : \frac{4}{28}$

$= 7 : 32$

$\therefore$ Ratio of molecules of O_2 and N_2 = 7 : 32

B56. (*c*) 1000 mL of 0.001 M HCl contain Cl^- ions

$= 0.001$ mol

100 mL of 0.001 M HCl will contain Cl^- ions

$= \frac{0.001}{1000} \times 100$

$= 10^{-4}$ mol

No. of Cl^- ions = $10^{-4} \times 6.022 \times 10^{23} = 6.022 \times 10^{19}$

B57. (*b*) Percentage of C = $\frac{12}{44} \times \frac{0.44}{0.30} \times 100 = 40\%$

Percentage of H = $\frac{2}{18} \times \frac{0.18}{0.30} \times 100 = 6.67\%$

Percentage of O = 100 – (40 + 6.67) = 53.33%

Calculation of empirical formula

Element	Percentage composition	At. mass	Moles of atoms	Mole ratio or atomic ratio
C	40	12	40/12 = 3.33	1
H	6.67	1	6.67/1 = 6.67	2
O	53.33	16	53.33/16 = 3.33	1

Empirical formula = CH_2O

Empirical formula mass = $12 + 2 \times 1 + 16 = 30$

Molecular mass = 60

$\therefore \quad n = \frac{60}{30} = 2$

$\therefore$ Molecular formula = $(CH_2O)_2 = \mathbf{C_2H_4O_2}$

B58. (*a*) : 6.022×10^{23} molecules of oxygen = 32 g

1.8×10^{22} molecules of oxygen = $\frac{32}{6.022\times10^{23}} \times 1.8 \times 10^{22}$

$= 0.956$ g $\approx$ **0.96 g**

B59. (*b*) : $CH_3—CH=CH_2 + \frac{9}{2} O_2 \longrightarrow 3CO_2 + 3H_2O$ (Propene)

3 mol (or 54g) of water are obtained from 1 mol (42g) of propene

or 54g of water is obtained from propene = 42 g

27g of water is obtained from propene

$= \frac{42}{54} \times 27 = 21$ g

B60. (*e*) : 2.46g of hydrated salt ($MSO_4.xH_2O$) gives anhydrous salt = 1.20 g

$\therefore$ Mass of water = 2.46 – 1.20 = 1.26 g

Percentage of water = $\frac{1.26}{2.46} \times 100 = 51.2\%$

Percentage of anhydrous salt = 100 – 51.2 = 48.8%

48.8 g of anhydrous salt contain water = 51.2 g

120 g (1 mol) of anhydrous salt contain water

$= \frac{51.2}{48.8} \times 120 = 126$ g

No. of water molecules = $\frac{126}{18} = 7$ molecules

B61. (*b*) : Mass of CCl_4 = Volume × Density

$= 500 \times 1.60 = 800$ g

Molar mass of naphthalene ($C_{10}H_8$)

$= 12 \times 10 + 1 \times 8 = 128$g mol^{-1}

Moles of naphthalene = $\frac{51.2}{128}$

Molality = $\frac{51.2\times1000}{128\times800} = 0.500$ m

B62. (*a*) : Moles of CO_2 = $\frac{4.4}{44} = 0.1$ mol

1 mol of CO_2 = 6.022×10^{23} molecules of CO_2

or = $2 \times 6.022 \times 10^{23}$ atoms of oxygen

$\therefore$ 0.1 mol of CO_2 = $2 \times 6.022 \times 10^{23} \times 0.1$

$= 1.2044 \times 10^{23}$

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B63. (*c*) :

Element	Percentage	Atomic mass	Moles	Simplest ratio
C	40.0	12	$\frac{40}{12} = 3.33$	3.33/3.33=1
H	13.33	1	$\frac{13.3}{1} = 13.33$	13.33/3.33=4
N	46.67	14	$\frac{46.67}{14} = 3.33$	3.33/3.33=1

Empirical formula = CH_4N

B64. (*b*) : $C_xH_y + \left(x + \frac{y}{4}\right) O_2 \longrightarrow xCO_2 + \frac{y}{2} H_2O$

15mL $15\left(x + \frac{y}{4}\right)$

0 0 $15x$ mL

Volume of oxygen used,

$Vo_2 = \frac{20 \times 375}{100} = 75mL$

$15\left(x + \frac{y}{4}\right) = 75$

$\left(x + \frac{y}{4}\right) = 5$

This corresponds to formula C_3H_8.
It may be noted that in this case the further information i.e, 330 mL volume is neglected. If we use that information then none of the answer is correct.

B65. (*c*) : Maximum volume of 3M HCl solution can be prepared by taking 500 mL of 2N HCl and x mL of 5 N HCl so that total volume becomes $(500 + x)$ mL

For HCl, molarity = normality

Applying $N_1V_1 + N_2V_2 \equiv N_3V_3$

$500 \times 2 + x \times 5 \equiv (500 + x) \times 3$

$1000 + 5x = 1500 + 3x$

$2x = 500$ or $x = 250$ mL

Thus, maximum volume of 3 M solution formed

$= 500 + 250 = 750$ mL

B66. (*d*) : Equivalents of acid = Equivalents of base

1000 mL of base = 0.1 equivalent

20 mL of base $= \frac{0.1}{1000} \times 20 = 2 \times 10^{-3}$

Equivalents of acid $= 2 \times 10^{-3}$

Gram equivalents $= \frac{\text{Mass}}{\text{Equivalent wt}}$

$2 \times 10^{-3} = \frac{0.126}{\text{Equivalent wt}}$

$\therefore$ Equivalent wt $= \frac{0.126}{2 \times 10^{-3}} = 63$

B67. (*c*) : Let mass of $CH_4(g)$ = 1 g

Moles of CH_4 (*g*) $= \frac{1}{16}$

Molecules of CH_4 (g) $= \frac{1}{16} \times 6.022 \times 10^{23}$

Mass of SO_2 (g) = 2g

Moles of SO_2 (g) $= \frac{2}{64}$

Molecules of $SO_2 = \frac{2}{64} \times 6.022 \times 10^{23}$

Ratio of number of molecules of SO_2(g) and CH_4(g)

$\frac{2}{64} \times 6.022 \times 10^{23} : \frac{1}{16} \times 6.022 \times 10^{23}$

$\frac{1}{32} : \frac{1}{16}$ or 1 : 2

B68. (*b*) : Equivalents of HCl $= \frac{y}{1000} \times x = xy \times 10^{-3}$

Equivalents of NaOH $= \frac{x}{1000} \times y = xy \times 10^{-3}$

	HCl	+ NaOH	$\longrightarrow$ NaCl	+ H_2O
Equivalents added	$xy \times 10^{-3}$	$xy \times 10^{-3}$	0	0
Equivalents left	0	0	$xy \times 10^{-3}$	$xy \times 10^{-3}$

Equivalents of NaCl present in $(x + y)$ mL solution = $xy \times 10^{-3}$

Volume of water added = $(x + y)$ mL

Total volume of solution = $(x + y) + (x + y)$ mL

Normality $= \frac{xy \times 10^{-3}}{(x+y)+(x+y)} \times 1000$

$= \frac{xy}{2(x+y)}$ N

B69. (*a*) : No. moles of H_2SO_4 in 98 mg $= \frac{98 \times 10^{-3}}{98} = 1 \times 10^{-3}$

No. of moles of 3.01×10^{20} molecules of

$H_2SO_4 = \frac{3.01 \times 10^{20}}{6.022 \times 10^{23}}$

$= 0.5 \times 10^{-3}$

Moles of H_2SO_4 left = $1 \times 10^{-3} - 0.5 \times 10^{-3} = 0.5 \times 10^{-3}$

B70. (*e*) : $MgCO_3 \xrightarrow{\text{Heat}} MgO + CO_2$

10g 4g 0.1 mol

Molar mass of $MgCO_3$ = 24 + 12 + 3 × 16

= 84 g mol^{-1}

Molar mass of MgO = 24 + 16 = 40 g mol^{-1}

40 g of MgO is obtained from 84 g of $MgCO_3$

4 g of MgO will be obtained from $= \frac{84}{40} \times 4$

= 8.4 g of $MgCO_3$

$\therefore$ Percentage purity $= \frac{8.4}{10} \times 100 = 84\%$

B71. (*c*) : Molar mass of Na_2CO_3 = 2 × 23 + 12 + 3 × 16

= 106 g mol^{-1}

$Na_2CO_3 . x\ H_2O$ has 50% H_2O by mass

$(106 + 18x) \times \frac{50}{100} = 18x$

$53 + 9x = 18x$

$9x = 53$ or $x = 5.88 \approx 6$

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B72. (*b*) : $M_2CO_3 + 2HCl \longrightarrow 2MCl + H_2O + CO_2$

1g 0.01186 mol

No. of moles of M_2CO_3 = No. of moles of CO_2

$$\frac{1}{M} = 0.01186$$

$$M = \frac{1}{0.01186} = 84.3$$

Molar mass of M_2CO_3 = 84.3 $gmol^{-1}$

B73. (*a*) : Mass of $Co(NO_3)_2 \cdot 6H_2O$ = 30g

Molar mass = 59 + 2 × 14 + 12 × 16 + 12 × 1 = 291

Moles of $Co(NO_3)_2 \cdot 6H_2O = \frac{30}{291}$

$$\text{Molarity} = \frac{30}{291 \times 4.3} = 0.024 \text{ M}$$

B74. (*d*) : Mass of an electron = 9.108×10^{-31} kg

Mass of 1 mol of electrons = $9.108 \times 10^{-31} \times 6.023 \times 10^{23} = 9.108 \times 6.023 \times 10^{-8}$ kg

$$\text{No. of moles in 1 kg} = \frac{1}{9.108 \times 10^{-8} \times 6.023 \times 10^{23}}$$

$$= \frac{1}{9.108 \times 6.023 \times 10^{23}} \times 10^8$$

B75. (*b*) : According to Dulong-Petit's law

Approx. at. mass × sp. heat = 6.4

$$\therefore \text{ At. mass (approx)} = \frac{6.4}{0.16} = 40$$

Let formula of metal chloride = MCl_x

$$\% \text{ Chlorine} = \frac{35.5 \times x \times 100}{40 + 35.5x}$$

or $$\frac{35.5x \times 100}{40 + 35.5x} = 65$$

$$\frac{35.5x}{40 + 35.5x} = \frac{65}{100}$$

or $$\frac{40}{35.5x} + 1 = \frac{100}{65}$$

$$\frac{40}{35.5x} = \frac{100}{65} - 1 = \frac{35}{65}$$

$$\frac{40}{35.5x} = \frac{7}{13}$$

$$35.5x = \frac{40 \times 13}{7}$$

$$x = \frac{40 \times 13}{7 \times 35.5} = 2.09 \simeq 2$$

Formula = MCl_2

B76. (*b*) : $2Mg + O_2 \longrightarrow 2\,MgO$

$$\text{Moles of Mg} = \frac{1.0}{24} = 0.042$$

$$\text{Moles of } O_2 = \frac{0.28}{32} = 0.00875$$

1 mol of O_2 requires Mg = 2 mol

0.00875 mol of O_2 requires Mg = 2 × 0.00875 = 0.0175

$\therefore$ Mg is in excess.

Moles of Mg left in excess = 0.042 − 0.0175 = 0.0245

Mass of Mg left in excess = 0.0245 × 24 = 0.58 g

B77. (*a*) : $2\overset{+2}{Fe}SO_4 \longrightarrow 2\overset{+3}{Fe}_2(SO_4)_3$

Change in oxidation state per Fe atom is 1.

$\therefore$ Equivalent wt. = Atomic wt. = 55.84 g mol^{-1}

B78. (*a*) : Ethanol : C_2H_5OH

Molecular mass = 2 × 12 + 6 × 1 + 16 × 1 = 46

$$\text{Mass \% C} = \frac{\text{Mass of C}}{\text{Molecular mass}} \times 100$$

$$= \frac{24}{46} \times 100 = 52\%$$

B79. (*d*) :

Element	Relative mass	Relative mole	Simplest whole no. ratio
C	6	6/12 = 0.5	1
H	1	1/1 = 1	2

$\therefore$ $x = 1$ and $y = 2$

Combustion of C_xH_y

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \left(\frac{y}{2}\right)H_2O$$

Oxygen atoms required for complete combustion of C_xH_y

$$= 2\left(x + \frac{y}{4}\right)$$

$$z = \frac{1}{2}\left[2\left(x + \frac{y}{4}\right)\right] = x + \frac{y}{4}$$

$$z = 1 + \frac{2}{4} = \frac{3}{2}$$

Ratio of $x : y : z = 1 : 2 : \frac{3}{2}$

$= 2 : 4 : 3$

Formula : $C_2H_4O_3$

B80. (*a*) : $\text{Moles of NaOH} = \frac{8}{40} = 0.2$ mol

$$\text{Moles of water} = \frac{18}{18} = 1.0 \text{ mol}$$

$$\text{Mole fraction of NaOH} = \frac{0.2}{0.2 + 1.0} = 0.167$$

$$\text{Molality} = \frac{0.2 \times 1000}{18} = 11.11 \text{ m}$$

B81. (*a*) : $\text{Molarity} = \frac{\text{Moles of sugar}}{\text{Vol. of solution in L}}$

$$0.1 = \frac{\text{Moles of sugar}}{2 \text{ L}}$$

Moles of sugar = 0.1 × 2 = 0.2 mole

Mass of sugar = 0.2 × 342

= 68.4 g

B82. (*c*) : Moles of $Na^+ = \frac{92}{23} = 4$

$$\text{Molality} = \frac{4}{1} = 4 \text{ m}$$

B83. (*b*) : Atomic mass of iron

$$= \frac{54 \times 5 + 56 \times 90 + 57 \times 5}{100}$$

$$= \frac{270 + 5040 + 285}{100} = 55.95$$

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C. *mcq with more than one correct answers*

C1. (*a, d*) : Mole fraction and molality are independent of temperature.

C2. (*a, d*) : Moles of water = $\frac{25}{18}$ = 1.388

Moles of ethanol = $\frac{25}{46}$ = 0.543

Moles of acetic acid = $\frac{50}{60}$ = 0.833

Total moles = 1.388 + 0.543 + 0.833 = 2.764

x (water) = $\frac{1.388}{2.764}$ = 0.502

x (ethanol) = 0.196

x (acetic acid) = 0.302

x(ethanol) + x(acetic acid) = 0.498.

C3. (*a, b, d*) : 8g of O_2 = $\frac{8}{32}$ = 0.25 mol

No. of O atom = 0.25 × 2 × N_A = 0.5 N_A

(*a*) 11 g of CO_2 = $\frac{11}{44}$ = 0.25 mol

No. of O atoms = 2 × 0.25 × N_A = 0.5 N_A

(*b*) 14 g of CO = $\frac{14}{28}$ = 0.5 mol

No. of O atoms = 0.5 × N_A = 0.5 N_A

(*c*) 32 g of SO_2 = $\frac{32}{64}$ = 0.5 mol

No. of O atoms = 0.5 × 2 × N_A = 1.0 N_A

(*d*) 8 g of O_3 = $\frac{8}{48}$ = 0.166 mol

No. of O atoms = 0.166 × 3 × N_A

= 0.5 N_A

So, *a*, *b* and *d* have same number of O atoms.

C5. (*b, c*) : Molar mass of $MgSO_4$ = 24 + 32 + 4 × 16 = 120

% mass of Mg = $\frac{24}{120}$ × 100 = 20%

% mass of S = $\frac{32}{120}$ × 100 = 26.7%

C6. (*b, c*) : If N_A is Avogadro's number

(*i*) 14g (*ii*) 40 g

(*iii*) $\frac{108}{6.022\times10^{23}}$ = 1.79 × 10^{-22}g

(*iv*) 32 g (*v*) 1.99 g (*vi*) 1g

So (*b*) and (*c*) are correct.

C7. (*c, d*) : Molarity and normality depends on temperature.

D. *mcq based on comprehension*

D1. (*b*) : Molar mass of $C_{10}H_8$ = 10 × 12 + 8 × 1 = 128

Mass of 10 molecules of $C_{10}H_8$ = $\frac{128}{6.02\times10^{23}}\times10$

= 2.12 × 10^{-21} g

D2. (*b*) : $\frac{32\times10^{20}}{6.02\times10^{23}}$ = 5.32 × 10^{-3} g

D3. (*a*) : $\frac{107.81}{6.02\times10^{23}}\times10^6$ = 1.79× 10^{-16} g

D4. (*c*) : % Fe = $\frac{4\times55.85}{\text{Mol. mass of haemoglobin}}$

$\therefore$ Mol. mass = $\frac{4\times55.85\times100}{0.335}$ = 66687

or = 66800

D5. (*c*) : $\frac{0.29}{78.96}$ = 3.672 × 10^{-3}

D6. (*a*) : Mol. mass = $\frac{1\times55.85\times100}{0.376}$

= 14853 ≃ 14850

D7. (*b*) : Mol. mass of peroxidase = $\frac{1\times78.96\times100}{0.29}$

= 27228

No. of atoms in 1 μg = $\frac{27228}{6.022\times10^{23}}\times10^{-6}$

= 4.52 × 10^{14}

D8. (*b*) : Mol. mass of haemoglobin = 66800 (Q.C4)

Moles of haemoglobin = $\frac{1\times10^{-3}}{66800}$

= 1.497 × 10^{-8}

Moles of iron = 1.497 × 10^{-8} × 4

= 5.99 × 10^{-8} ≈ 6.0 × 10^{-8}

D9. (*c*): 100 g of 109% oleum on dilution gives 109 g H_2SO_4 solution, and the SO_3 present in 100 g oleum will combine with 9 g water as

$$H_2O + SO_3 \longrightarrow H_2SO_4$$

Moles of water added = $\frac{9}{18}$ = Moles of free SO_3 present

$\therefore$ Mass of SO_3 = $\frac{9}{18}$ × 80 = 40 g

% of SO_3 = $\frac{40}{100}$ × 100 = 40%

D10. (*a*): 100 g of oleum on dilution gives 112 g H_2SO_4

Wt. of H_2SO_4 after dilution = 112 g

Wt. of water added = 12 g

Moles of H_2O = $\frac{12}{18}$ = 0.67 = Moles of free SO_3

Wt. of SO_3 = 0.67 × 80 = 53.6

% of SO_3 = 53.6 %, % of H_2SO_4 = 46.4

Integer Type and Numerical Value Type Questions

● **1.** (7) : 1.420 g of anhydrous $ZnSO_4$ combine with water

= 2.528 – 1.420

= 1.108 g

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∴ 161.5 g of anhydrous $ZnSO_4$ combines with

water $= \frac{1.108}{1.420} \times 161.5$

$= 126$

No. of moles of water $= \frac{126}{18} = 7$

No. of water molecules in the salt = 7

● **2.** (7) : $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

Moles of CO used $= \frac{294}{28} = 10.5$

3 mol of CO are used to make = 2 mol of Fe

10.5 mol of CO are used to make $= \frac{2}{3} \times 10.5 = 7$

● **3.** (6) : Empirical formula comes out to be CH

Empirical formula mass = 12 + 1 = 13

Molecular mass = 2 × 39 = 78

$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$

$= \frac{78}{13} = 6.$

● **4.** (6) : $M_1V_1 + M_2V_2 \equiv M_3V_3$

$10 \times 428 + 3 \times 572 = M_3 \times 1000$

∴ $M_3 = 6$

● **5.** (7) : $\text{Density} = \frac{\text{Mass}}{\text{Volume}}$

10.5 g/cm^3 means 10.5 g of Ag is present in 1 cm^3

No. of Ag atoms in 1 cm^3 $= \frac{10.5}{108} \times 6.02 \times 10^{23}$

$= 5.85 \times 10^{22}$

No. of atoms in 1 cm $= (58.5 \times 10^{21})^{1/3}$

$= 3.882 \times 10^7$

No. of atoms in 1 cm^2 $= (3.882 \times 10^7)^2$

No. of atoms in 10^{-12}m^2 or 10^{-8} cm^2

$= (3.882 \times 10^7)^2 \times 10^{-8}$

$= 1.506 \times 10^7$

∴ Value of $x = 7$

● **6.** (3) : According to charge balance

$n(+2) + 2(+3) + 6(+4) + 18(-2) = 0$

$2n = 6$

or $n = 3$

● **7.** (5) : $3Br_2 + 3Na_2CO_3 \rightarrow 5NaBr + NaBrO_3 + 3CO_2$

● **8.** (8) : 29.2% (*w*/*w*) HCl means that 29.2g of HCl is present in 100g of solution.

Volume of HCl solution $= \frac{100}{1.25} = 80\text{g}$

Molarity of solution $= \frac{29.2/36.5}{80} \times 1000$

$= 10\text{M}$

Applying $M_1V_1 = M_2V_2$

$10 \times V_1 = 200 \times 0.4$

$V_1 = \frac{200 \times 0.4}{10} = 8$

● **9.** (4) : Boltzmann constant,

$k = \frac{\text{Gas constant, R}}{\text{Avogadro number, N}_A}$

or $R = k \times N_A$

$= 1.380 \times 10^{-23} \times 6.023 \times 10^{23}$

Since both the terms have 4 significant figures. The number of significant figures in the term having least number of significant figures is 4. No. of significant figures in calculated value will be 4.

●**10.** (126.00) :

$2MnCl_2 + 5K_2S_2O_8 + 8H_2O \longrightarrow 2KMnO_4 + 4K_2SO_4 + 6H_2SO_4 + 4\,HCl$ ...(*i*)

$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10\,CO_2$ ...(*ii*)

Mass of oxalic acid added = 225 mg

Moles of oxalic acid $= \frac{225 \times 10^{-3}}{90}$

$= 2.5 \times 10^{-3}$

From equation (*ii*)

Moles of $KMnO_4$ react with 5 mol of $H_2C_2O_4$ = 2 mol

Moles of $KMnO_4$ react with 2.5×10^{-3} mol of $H_2C_2O_4 = \frac{2}{5} \times 2.5 \times 10^{-3} = 1 \times 10^{-3}$ mol

Moles of $MnCl_2$ required initially = 1×10^{-3} mol

Mass of $MnCl_2$ required initially = $1 \times 10^{-3} \times 126$

= 126 mg

NCERT Exemplar Problems: MCQs Type I

1. (*b*) : Average reading of student A $= \frac{3.01 + 2.99}{2} = 3.00$

Average reading of student B $= \frac{3.05 + 2.95}{2} = 3.00$

Correct reading = 3.0

For both the students average value is same as the correct value. Hence readings of both the students are correct. But the readings of student A are close to each other (differ only by 0.02) and hence readings of student A are precise. Thus, results of student A are both precise and accurate.

2. (*c*) : $°C = \frac{5}{9}[°F - 32]$

$= \frac{5}{9} \times (200 - 32)$

$= 93.3°C$

3. (*c*) : $\text{Molarity} = \frac{5.85/58.5}{500} \times 1000$

$= 0.2 \text{ mol L}^{-1}$

4. (*b*) $M_1V_1 = M_2V_2$

$5\text{ M} \times 500\text{ mL} = M_2 \times 1500\text{ mL}$

∴ $M_2 = \frac{5 \times 500}{1500} = 1.66\text{ M}$

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Competition File

5. (*d*) : 4 g He = $\frac{4}{4}$ = 1 mol = N_A atoms.

46 g Na = $\frac{46}{23}$ = 2 mol = $2N_A$ atoms.

0.40 g Ca = $\frac{0.40}{40}$ = 0.01 mol = 10^{-2} N_A atoms.

12 g He = $\frac{12}{4}$ = 3 mol = 3 N_A atoms.

Thus, 12 g of He contain maximum number of atoms.

6. (*c*) Molar mass of glucose ($C_6H_{12}O_6$)

$= 6 \times 12 + 1 \times 12 + 6 \times 16 = 180$

$$\text{Molarity} = \frac{0.9}{180 \times 1} = 0.005 \text{ M.}$$

7. (*d*) $$\text{Molality} = \frac{\text{Moles of HCl}}{\text{Mass of water (in g)}} \times 1000$$

$$= \frac{18.25/36.5}{500} \times 1000 = 1 \text{ m.}$$

8. (*a*) : $$\text{Moles of } H_2SO_4 = \frac{0.02}{1000} \times 100 = 0.002 \text{ mole}$$

$$\text{Molecules} = 0.002 \times 6.022 \times 10^{23}$$

$$= 12.044 \times 10^{20}$$

9. (*b*) : Molar mass of $CO_2 = 12 + 2 \times 16 = 44$

$$\% \text{ carbon} = \frac{12}{44} \times 100 = 27.27\%$$

10. (*c*) : Empirical formula mass

$= 12 + 2 + 16 = 30$

$$n = \frac{\text{Molecular formula mass}}{\text{Empirical formula mass}}$$

$$= \frac{180}{30} = 6$$

Molecular formula = $(CH_2O)_6$

= $C_6H_{12}O_6$

11. (*a*) : Mass = 3.12 g mL^{-1} × 1.5 mL

∴ = 4.68 g

= 4.7

(upto 2 significant figures)

12. (*c*) A compound does not retain the physical properties of its constituent elements.

14. (*b*) Equation is not balanced.

15. (*b*) Statement (*b*) is correct according to law of conservation of mass.

NCERT Exemplar Problems: MCQs Type II

16. (*a*, *d*) 1 mole of O_2 at S.T.P.

= 6.022×10^{23} molecules of O_2

= 32 g of O_2.

17. (*b*, *c*) 1 L of 0.1 M H_2SO_4 contains = 0.1 mol H_2SO_4

1 L of 0.1 M NaOH contains = 0.1 mol NaOH

According to the given equation, 1 mol of H_2SO_4 reacts with 2 mol of NaOH. Therefore, 0.1 mol of NaOH will react with 0.1/2 = 0.05 mol of H_2SO_4 and 0.05 mol of H_2SO_4 will remain unreacted. Therefore, NaOH is the limiting reagent.

∴ 0.01 mol of NaOH will produce 0.05 mol Na_2SO_4

Molar mass of $Na_2SO_4 = 2 \times 23 + 1 \times 32 + 4 \times 16$

= 142

Mass of Na_2SO_4 formed = $0.05 \times 142 = 7.10$ g

Volume of solution after mixing = 2 L

H_2SO_4 left unreacted = 0.05 mol

$$\text{Molarity of solution} = \frac{0.05}{2} = 0.025 \text{ mol } L^{-1}$$

18. (*c*, *d*) 16 g O_2 = $\frac{16}{32}$ = 0.5 mol

= $2 \times 0.5 \times N_A$ atoms = N_A atoms

4 g H_2 = $\frac{4}{2}$ = 2 mol

= $2 \times 2 \times N_A$ atoms = 4 N_A atoms

44 g CO_2 = $\frac{44}{44}$ = 1 mol

= $3 \times 1 \times N_A$ atoms = 3 N_A atoms

28 g N_2 = $\frac{28}{28}$ = 1 mol

= $2 \times 1 \times N_A$ atoms = 2 N_A atoms

32 g O_2 = $\frac{32}{32}$ = 1 mol

= $1 \times 2 \times N_A$ atoms = 2 N_A atoms

12 g C = $\frac{12}{12}$ = 1 mol = N_A atoms

23 g Na = $\frac{23}{23}$ = 1 mol = N_A atoms

∴ (*c*) and (*d*) are correct

19. (*a*, *b*) Molar conc. of NaOH solution = $\frac{20/40}{200} \times 1000$

= 2.5 M.

Molar conc. of KCl solution = $\frac{0.5}{200} \times 1000 = 2.5$ M

Molar conc. of NaOH solution = $\frac{40/40}{100} \times 1000$

= 10 M

Molar conc. of KOH solution = $\frac{20/56}{200} \times 1000$

= 1.78 M

Thus, (*a*) and (*b*) have the same concentration.

20. (*c*, *d*) 16 g CO = $\frac{16}{28}$ = 0.57 mol = 0.57 N_A molecules

28 g N_2 = $\frac{28}{28}$ = 1.0 mol = N_A molecules

14 g N_2 = $\frac{14}{28}$ = 0.5 mol = 0.5 N_A molecules

1.0 g H_2 = $\frac{1.0}{2}$ = 0.5 mol = 0.5 N_A molecules.

NCERT Exemplar Problems: Assertion-Reason Type

25. (*a*) Both A and R are true and A is the correct explanation of A.

26. (*b*) Both A and R are true but R is not the answer of A.

27. (*c*) A is true but R is false.

28. (*c*) A is false but R is true.

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Unit Practice Test

for Board Examination

Time Allowed: 1 hr. ***Maximum Marks: 25***

1. Express decimal equivalent of 2/3 to three significant places. (1)

2. What is the mass of one ^{12}C atom in grams? (1)

3. Express the result of 12.26 + 16.0 + 1.089 to correct number of significant figures. (1)

4. Define limiting reagent. (1)

5. The human body temperature is 98.6°F. What is its value in °C and K ? (1)

6. One atom of an element weighs 9.75×10^{-23} g. Calculate its atomic mass. (2)

7. Round up the following to three significant figures :

(*i*) 10.4207

(*ii*) 0.04597

(*iii*) 5.000

(*iv*) 2808 (2)

8. The volume of a drop of rain was found to be 0.448 ml at N.T.P. How many molecules of water and number of atoms of hydrogen are present in this drop? (2)

9. (*i*) Calculate the amount of carbon dioxide that could be produced when 2 moles of carbon are burnt with 16 g of dioxygen.

(*ii*) How many atoms of He are present in 52 u of He? (3)

10. Calculate the amount of $KClO_3$ needed to supply sufficient oxygen for burning 112 L of CO gas at N.T.P. (3)

11. Commercially available sulphuric acid contains 93% acid by mass and has density of 1.84 g mL^{-1}. Calculate

(*i*) the molarity of the solution

(*ii*) volume of concentrated acid required to prepare 2.5 L of 0.50 M H_2SO_4. (3)

12. What is meant by empirical formula and molecular formula? How are they related to each other? Explain with an example. A compound on analysis gave the following percentage composition: Na = 14.31%, S = 9.97%, H = 6.22% and O = 69.50%. Calculate the molecular formula of the compound assuming that all the hydrogens in the compound is present in combination with oxygen as water of crystallisation. The molecular mass of the compound is 322. (5)

To check your performance, see HINTS and SOLUTIONS to some questions at the end of Part I of the book.

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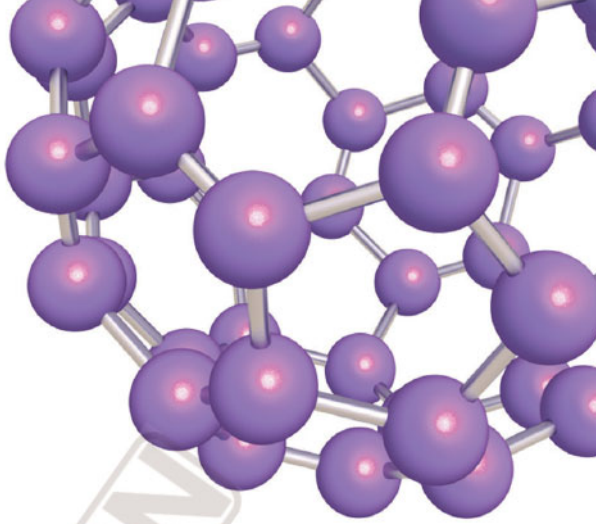
STRUCTURE OF ATOM



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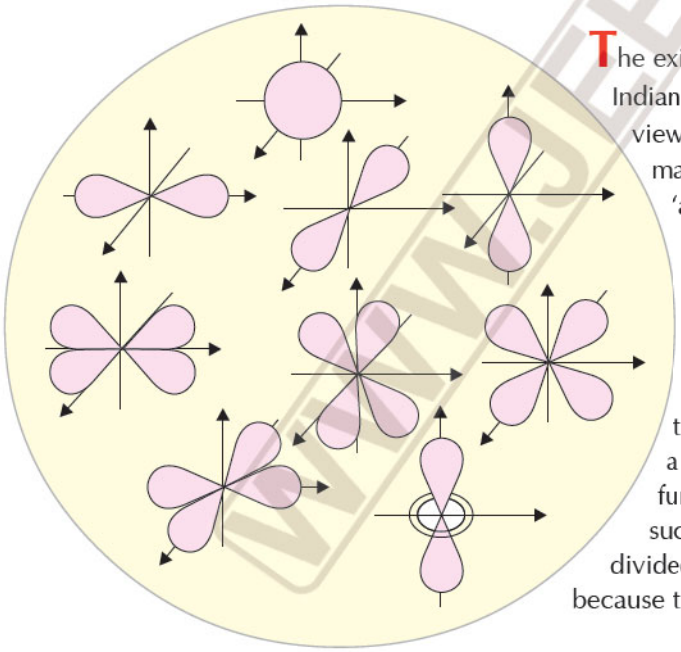

The existence of atoms has been proposed since the times of early Indian and Greek philosophers around 400 B.C., who were of the view that the atoms are the fundamental building blocks of matter. The word 'atom' has been derived from the Greek word '**a-tomio**' meaning **uncutable** or **non-divisible**.

The first definite theory about the structure of matter was put forward by John Dalton, in 1808, called **Daltonís atomic theory.** According to his theory, all matter are composed of extremely small, structureless, hard spherical particles called **atoms**. However, the discoveries towards the end of 19th and early 20th centuries showed that atom has a complex structure and is not indivisible. These studies further revealed that atom consists of still smaller particles such as ***electron, proton*** and ***neutron,*** into which it may be divided. These particles are regarded as **fundamental particles** because these are the main constituents of all atoms.

SUBATOMIC PARTICLES

Discovery of Electron : Study of Cathode Rays

The electron was discovered by J.J. Thomson at the end of 19th century during the studies of the passage of electricity through gases at extremely low pressures. These experiments were known as ***discharge tube experiments***. The experiment in its simplest form consists of a cylindrical hard glass tube (about 50 cm long) closed

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at both ends [Fig.1]. It is known as **discharge tube** or **Crookes tube.** It is fitted with two metallic electrodes. The tube is connected to a side tube, through which it can be evacuated to any desired pressure with the help of a vacuum pump. The discharge tube is filled with the gas under study and the two electrodes are connected to a source of high voltage. The pressure of different gases could be adjusted by evacuation.

Under ordinary conditions, gases are poor conductors of electricity. However, when a sufficiently high voltage is applied across the electrodes, at very low pressures, the gases become conductors and electricity begins to flow in the form of rays. These rays are called **cathode rays.** The existence of these rays was shown by scientists like Plucker, Crookes, etc., but the main credit goes to J.J. Thomson. He studied the properties of cathode rays in detail which led to the discovery of an electron.

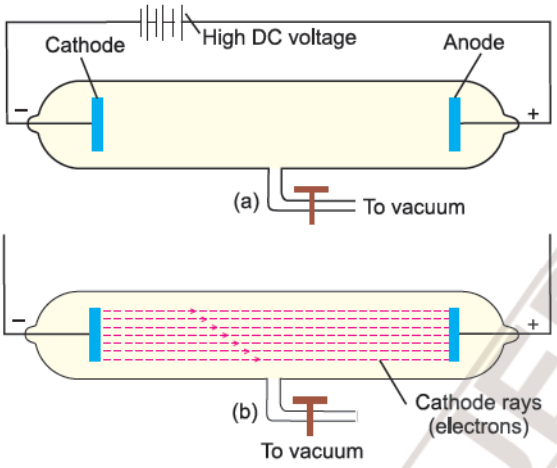

Fig. 1. Discharge tube experiments (*a*) Discharge tube containing a gas. (*b*) Emission of cathode rays at high voltage and low pressure.

These rays moved from the cathode towards the anode in the form of stream of particles. These rays were named **cathode rays** or **cathode ray particles** because they originate from the cathode. The flow of current from cathode to anode was further checked by making a hole in anode and coating the tube behind anode with fluorescent material zinc sulphide. When these rays after passing through anode strike the zinc sulphide coating, a bright spot on the coating is developed (same thing happens in a television set).

Properties of Cathode Rays

From the various experiments carried out by J.J. Thomson and others, the cathode rays have been found to possess the following properties :

1. *The cathode rays travel in straight lines.* These rays start from cathode and move towards anode. Whenever an object is placed inside the tube, it casts a shadow on the wall opposite to the cathode.

2. *These rays themselves are not visible* but their behaviour can be observed with the help of certain kinds of materials (fluorescent or phosphorescent) which glow when hit by them. It may be remembered that television tubes are also cathode tubes and television pictures result due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials.

3. *Cathode rays produce mechanical effects.* For example, when a small paddle wheel is placed between the electrodes, it starts rotating.

4. In the presence of electrical or magnetic field, the behaviour of cathode rays are similar to that expected from negatively charged particles, suggesting that the ***cathode rays consist of negatively charged particles called electrons.***

5. When the cathode rays are allowed to strike a thin metal foil, it gets heated up. Thus, the *cathode rays possess heating effect.*

6. The characteristics of cathode rays do not depend upon the nature of electrodes and the nature of gas present in the cathode ray tube.

The ratio of charge to mass i.e., charge /mass is same for all the cathode rays irrespective of the gas used in the tube. Thus, *we can conclude that electrons are basic constituents of all the atoms.*

All these observations led to the conclusion that cathode rays consist of negatively charged particles. These charged particles constituting the cathode rays were named **electrons**.

Charge and Mass of Electron

(*i*) Determination of charge to mass ratio (*e*/*m*) of electrons

In 1897, J.J. Thomson determined the ratio of the charge (e) of the electron to its mass (m) by measuring the deflection under the simultaneous influence of electric and magnetic fields, applied perpendicular to each other.

The charge/mass ratio, e/m was found to be:

$$\text{Charge/mass} = \frac{e}{m} = 1.76 \times 10^{11}\ \text{C/kg}$$

(*ii*) Determination of charge on the electron

The charge on the electron was measured by R.A. Millikan in 1909 by a method known as **oil drop method.** The charge on the electron was found to be

$$\text{Charge } (e) = 1.60 \times 10^{-19}\ \text{C (Coulomb)}$$

Calculation of the mass of the electron. From the values of e/m and e, the mass (m) of the electron was determined by dividing e by e/m. Thus,

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Charge/mass $(e/m) = 1.76 \times 10^{11}$ C kg^{-1}

Charge $(e) = 1.60 \times 10^{-19}$ C

$$\text{Mass of electron } (m) = \frac{e}{e/m} = \frac{1.60 \times 10^{-19}\text{C}}{1.76 \times 10^{11}\text{C kg}^{-1}}$$

$$= 9.10 \times 10^{-31}\text{kg}$$

The mass of the electron is much smaller than the mass of an atom of hydrogen. It has been found that the mass of an electron is approximately 1/1837th (or 5.45×10^{-4} times) the mass of an atom of hydrogen.

However, *this mass is very small and for all practical purposes, it may be taken as negligible.* The charge of the electron is the smallest known electrical charge and is usually referred to as *unit negative charge.*

Thus, an **electron** may be defined as

a sub-atomic particle which carries one unit negative charge (1.6022×10^{-19} C) and has a mass (9.10×10^{-31} kg) equal to 1/1837th of that of hydrogen atom.

LEARNING PLUS

❑ Thomson's Experiment for Determination of Charge/Mass (e/m) of the electron

The apparatus is shown in Fig. 2. A high potential is maintained between the cathode and the anode. Electrons emitted from the cathode are accelerated by the high voltage. The circular disc after the anode selects the beam moving in a straight line. The beam then passes through electric and magnetic fields which are perpendicular to each other and also to the direction of the motion. Thomson suggested that the amount

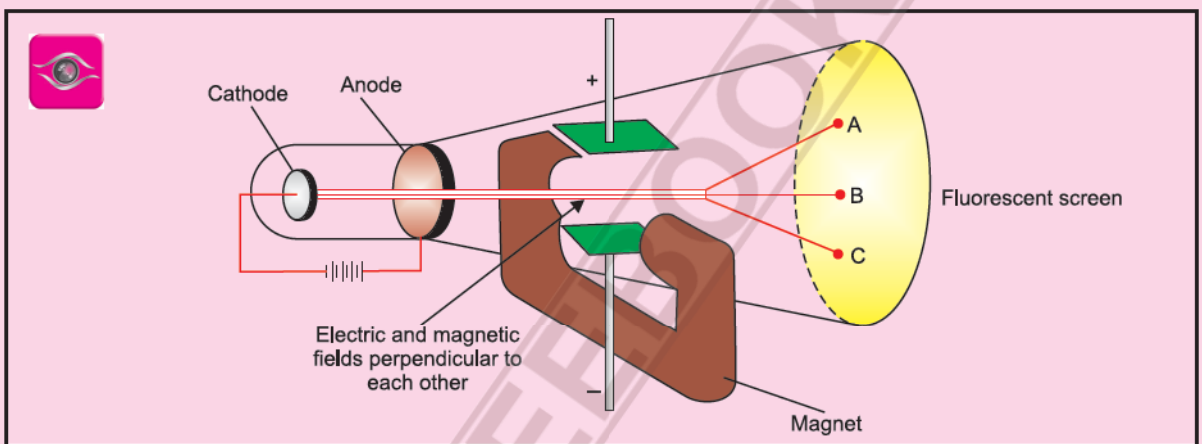

Fig. 2. Apparatus for determining the ratio of electric charge (e) to mass (m) of electrons.

of deviation of the particles from their path in the presence of electrical and magnetic fields depends upon the charge on the electrons, mass of the electrons and strengths of the electric and magnetic fields.

When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A. Similarly, when only magnetic field is applied, electrons deviate from their path and hit the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron to the path followed as in the absence of electric or magnetic field and they hit the screen at point B. By carrying out accurate measurements on the deflections observed by electron on the electric field strength or magnetic field strength, Thomson was able to calculate the value of charge / mass ratio *i.e,* e/m. The value of e/m was found to be

$$e/m = 1.758820 \times 10^{11}\text{ C kg}^{-1}$$

or $$= \mathbf{1.76 \times 10^{11}\text{ C kg}^{-1}}$$

where m is the mass of electron in kg and e is the magnitude of the charge on the electron in Coulombs (C). Since electrons are negatively charged, the charge on electron is negative, $-e$.

The relative strengths of electric and magnetic fields and the ratio e/m control the deflections. Hence, by measuring the deflection and the field strength, e/m can be calculated.

❑ Determination of charge on the electron.

The charge on the electron was measured by R.A. Millikan in 1909 by a method known as **oil drop method.** The apparatus used is shown in Fig 3. Small drops of oil in the form of mist are formed by a sprayer and these are allowed to fall in between two metal plates, which could be electrically charged. A single drop between the plates is observed by means of a telescope equipped with a micrometer eye piece. The oil in the form of mist drop falls through the air under the influence of gravitational force. He then irradiated the space between the

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plates with X-rays. These knocked electrons out of some of the molecules of the air and some of these electrons, were caught by oil droplets which acquired electrical charge. By charging the upper plate positive and the lower plate negative, the oil drop experiences electric field in the upper direction. By adjusting the electrical field strength, the upward electrical field on the oil droplet was balanced against the downward gravitational force. Under these conditions, the drop remains stationary. From the amount of charge on the plates and the mass of the droplet, the charge on the droplet was determined. The mass of the droplet was determined from the rate of fall of droplet through the air when the plates were uncharged.

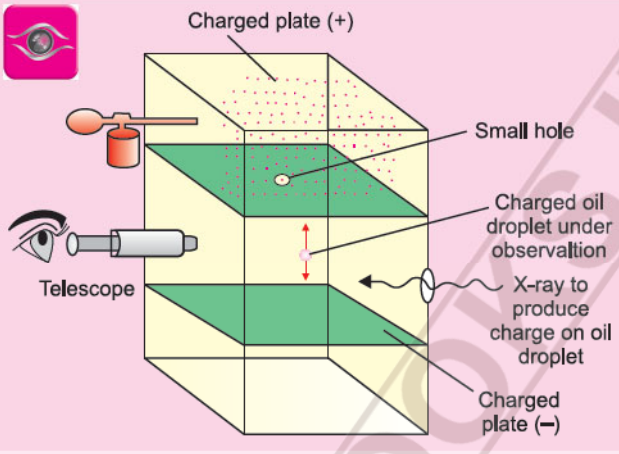

Fig. 3. Millikan's experiment for the determination of charge of electron.

From his experiments, Millikan found the charge of the electron to be **1.6022×10^{-19} coulombs.**

Discovery of Proton: Study of Anode Rays

The presence of negatively charged electrons in an atom suggests that there must be some positively charged particles because the atom on the whole is electrically neutral. In 1836, E. Goldstein discovered that in addition to cathode rays, a new kind of rays are also found streaming behind the cathode in discharge tube experiments (Fig. 4). These rays travelled in opposite direction to the cathode rays.

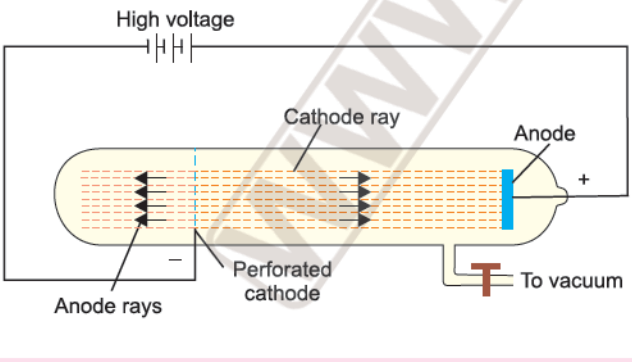

Fig. 4 Generation of anode rays (protons).

These rays are also deflected by the magnetic and electric fields like cathode rays. But the deflection of anode rays is in the opposite direction to that of cathode rays. This means that these rays consist of positively charged particles and were also named **positive rays** or **canal rays** or **anode rays.**

Characteristics of Anode Rays

Some of the characteristics of anode rays are :

1. The anode rays travel in straight lines and cast shadow of the object placed in their path.

2. The anode rays are deflected by the magnetic and electric fields like cathode rays. But the deflection of anode rays is in the opposite direction to that of the cathode rays. For example, these rays are attracted towards the negative plate in the electric field. This means that these rays consist of positively charged particles.

3. Like cathode rays, these rays also rotate the wheel placed in their path and also have heating effect.

4. The charge to mass ratio (e/m) for these rays is considerably smaller than electrons.

5. Unlike cathode rays, the e/m ratio of positive rays depends upon the nature of the gas taken in the tube.

The Charge and Mass of Particles Constituting Anode Rays

Unlike cathode rays, the charge to mass (e/m) ratio of anode rays was found to depend upon the nature of the gas taken in the discharge tube. **In case of hydrogen, the charge to mass *(e/m)* ratio was maximum.** The value was found to be **9.58×10^7 coulombs per kg.** Its charge has been found to be **1.6022×10^{-19} coulombs** which is equal in magnitude but opposite in sign to that of an electron *i.e.*, it has one unit of positive charge.

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Since e/m is maximum for hydrogen, the mass (m) of the positive particle obtained from hydrogen is the smallest. Its mass can be calculated from the values of e and e/m as :

$$m = \frac{e}{e/m} = \frac{1.6022 \times 10^{-19}\ \text{C}}{9.58 \times 10^{7}\ \text{C kg}^{-1}} = \mathbf{1.67 \times 10^{-27}\ kg}$$

This mass is about 1837 times the mass of an electron. This lightest positively charged particle was named proton and is also regarded as a fundamental particle. Thus, a **proton** is

a sub-atomic particle which carries one unit positive charge (1.6022×10^{-19} coulombs) and has mass (1.67×10^{-27} kg) equal to that of an atom of hydrogen.

LEARNING PLUS

❑ Discovery of Radioactivity

The discovery of cathode rays and anode rays showed that atoms are divisible into subatomic particles. This was further supported by the discovery of radioactivity by a French scientist Henri Becquerel in 1896.

Radioactivity** is the **phenomenon of spontaneous emission of active radiations by certain elements.

The substances which emit such radiations are called **radioactive substances.** The common radioactive substances are uranium, radium, polonium, thorium, etc.

The effect of magnetic and electric fields on these radiations was studied by placing a small sample of radioactive substance, uranium, in a cavity of a block of lead. The radioactive radiations coming out from a narrow slit were allowed to pass through a strong electric or magnetic field. The deflections of these rays were recorded on a photographic plate as shown in Fig. 5. The radiations were found to split into three types of rays. These were :

(*i*) **Alpha (α) rays.** *The rays which are deflected towards the negative electrode* are called **alpha (α) rays.** *These rays were found to consist of positively charged He^{2+} particles.* Each particle has a mass of 4 a.m.u. (m = 6.6 × 10^{-24}g) and carries two units of positive charge, +2 (e = 3.20 × 10^{-19} Coulomb).

(*ii*) **Beta (β) rays.** *The rays which are deflected towards the positive electrode are called* **beta (β) rays.** These are negatively charged particles which have the same e/m value as the cathode rays. Therefore, *β-rays were considered to be the streams of electrons.*

(*iii*) **Gamma (γ) rays.** *The rays which are not deflected at all and are therefore, neutral are called* **gamma (γ) rays.** These rays were regarded as high energy electromagnetic radiations having no charge and negligible mass.

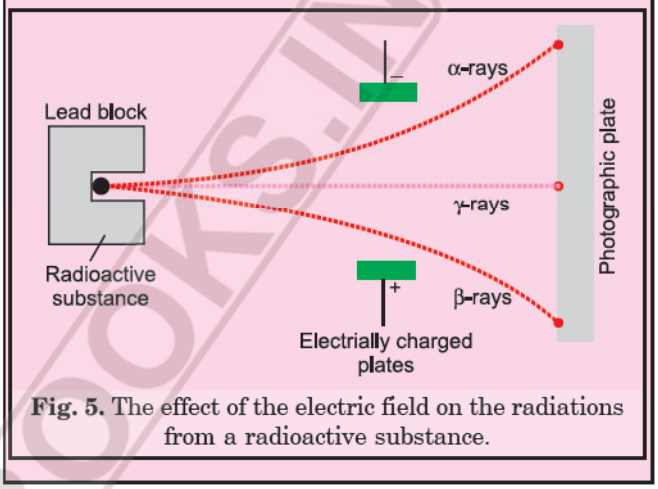

Fig. 5. The effect of the electric field on the radiations from a radioactive substance.

Discovery of Neutron

After the discovery of electron and proton, a need was felt for the presence of electrically neutral particle as one of the constituent of atom. The neutral particle, called neutron, was discovered by Chadwick and it helped to explain the atomic mass of atoms.

Chadwick, in 1932 bombarded a thin sheet of beryllium element with α-particles and observed highly penetrating rays which consist of streams of neutral particles. The neutral particles were found to have mass of 1.675 × 10^{-27} kg which is *nearly the same as that of hydrogen atom* and have no charge. These were named **neutrons.**

$$\underset{}{^{9}_{4}\text{Be}} + \underset{\alpha\text{-particle}}{^{4}_{2}\text{He}} \longrightarrow \underset{}{^{12}_{6}\text{C}} + \underset{\text{Neutron}}{^{1}_{0}\text{n}}$$

Thus, *a* **neutron *is a sub-atomic particle having mass (1.675×10^{-27} kg) equal to that of hydrogen atom and carrying no electrical charge.***

Thus, an atom consists of three fundamental particles; electron, proton and neutron. Their mass and charge are summarized below in Table 1.

ATOMIC MODELS

After the discovery of electron and proton, the scientists started thinking of arranging these particles in an atom. Different models were proposed to explain

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Table 1. Mass and charge of sub-atomic particles.

Particle	Mass (kg)	Relative mass (u)	Approximate mass (u)	Charge	Relative charge
Electron (e)	9.10939×10^{-31}	5.4858×10^{-4}	0	-1.6022×10^{-19} C	–1
Proton (p)	1.67262×10^{-27}	1.00737	1	$+1.6022 \times 10^{-19}$ C	+1
Neutron (n)	1.67493×10^{-27}	1.00867	1	0	0

REMEMBER

One unit charge = 4.80298×10^{-10} esu or = 1.60210×10^{-19} Coulombs

One u = $\frac{1}{12}$th the mass of C–12 or = 1.66056×10^{-27} kg

the distribution of subatomic particles in an atom. The first simple model was proposed by J.J. Thomson known as **Thomson's atomic model.**

THOMSON'S MODEL OF ATOM

J.J. Thomson proposed that an atom consists of a uniform sphere in which positive charge is uniformly distributed. The electrons are embeded into it in such a way as to give the most stable electrostatic arrangement (Fig. 6). The radius of the sphere is of the order of 10^{-10} m, which is equal to the size of the atom. This model was much like pudding or cake (of positive charge) with raisins (electrons) embedded into it. Therefore, this model is also known as **raisin pudding model.** This model was also compared with *water melon model* of positive charge in which seeds (electrons) are embedded. Therefore, this model is given different names such as *raisin pudding*, plum *pudding* or *watermelon model*.

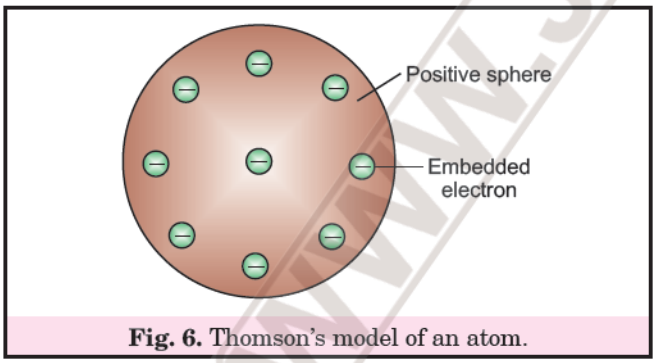

Fig. 6. Thomson's model of an atom.

This model was soon discarded, when Rutherford and his co-workers observed unusual scattering of α-particles by the thin metal foils.

RUTHERFORD'S SCATTERING EXPERIMENT: RUTHERFORD MODEL OF AN ATOM

In order to understand the arrangement of electrons and protons in an atom, Rutherford and his students (Hans Geiger and Ernest Masden) in 1909 performed a series of experiments known as **Rutherford's scattering experiments.** In their experiments, they bombarded a target of atoms by subatomic projectiles. These projectiles called **alpha (α) particles,** were obtained from a radioactive substance. Alpha particles are high energy positively charged helium ions having charge +2 and mass 4 u. They bombarded alpha (α) particles emitted from a radioactive substance on a piece of thin foil of gold or some other heavy metals.

In this experiment, a piece of radioactive substance (radium) is placed in a lead block (Fig. 7). The block is constructed in such a way with slits that only a narrow beam of α-particles could escape. The beam of high energy α-particles was directed at a thin gold foil (thickness about 100 nm). In order to detect the α-particles after scattering, a movable circular screen coated with zinc sulphide is placed around the gold foil.

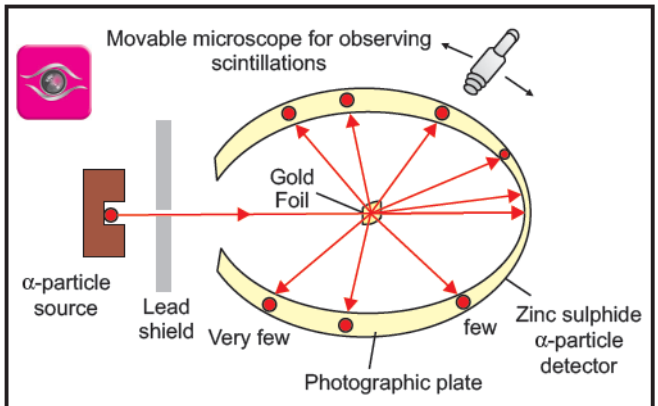

Fig. 7. Rutherford's α-particle scattering experiments.

When α-particles strike the zinc sulphide screen, these produce flashes of light or scintillations which can be detected. By examining different portions of the screen, it was possible to determine the proportions

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of the α-particles which got deflected through various angles. The following **observations** were made from these experiments :

(i) Most of the α-particles (nearly 99%) passed through the gold foil undeflected.

(ii) A small fraction of α - particles got deflected through small angles.

(iii) Very few (about one in 20,000) did not pass through the foil at all but suffered large deflections (more than 90°) or even came back suffering a deflection of 180°.

Now, according to Thomson's model, if the positive charge of the atom was uniformly distributed, then positively charged α-particles with a considerable mass (4 a.m.u.) would pass through weak electric field largely undeflected or slightly deflected. However, he noticed that some of the α-particles experienced strong deflections. Even some particles returned back from the foil. *Thus, Thomson's model could not provide answers for these observations and therefore, was discarded.*

Rutherford explained these observations as follows :

(i) Since most of the α-particles passed through the gold foil undeflected, *it means that there must be very large empty space within the atom.*

(ii) Alpha particles are positively charged and have considerable mass. They can be deflected only if they come close to some heavy positively charged mass due to enormous force of repulsion. Since some of the α-particles are deflected to certain angles, *it means that there is a heavy positively charged mass present in the atom. Moreover, this mass must be occupying a very small space within the atom because only a few α-particles suffered large deflections.*

(iii) The strong deflections or even bouncing back of α-particles from the foil, were explained to be *the direct collision with the heavy positively charged mass.*

The positively charged heavy mass which occupies only a small volume in an atom is called **nucleus.** It is supposed to be present in the centre of the atom.

All these types of deflections of α-particles from atoms are shown in Fig. 8. It is clear from the figure that the α-particles which pass at large distances from the nucleus do not suffer any deflections (marked *a*), those which pass close to the nucleus suffer small deflections (marked *b*), while very few which hit the nucleus are either deflected to large angles or they retraced their paths (marked *c*).

On the basis of the above experiments and observations, Rutherford proposed a model for the structure of the atom called *Rutherford's nuclear model of atom.*

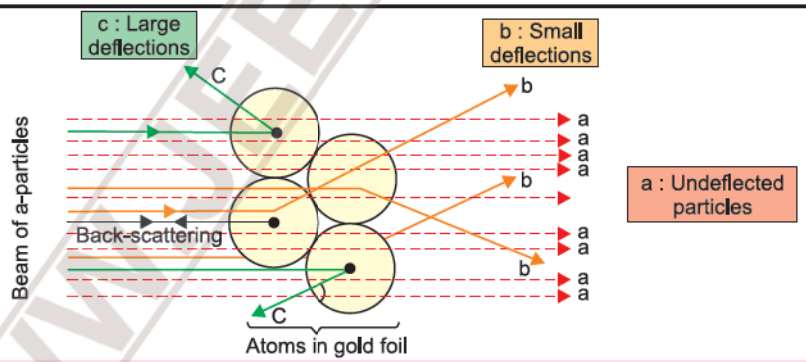

Fig. 8. Rutherford's model for deflections of α-particles.

Rutherford's Nuclear Model of Atom

The main features of this model are :

(i) In an atom, the entire mass and the positive charge is concentrated in extremely small region at the centre known as **nucleus.** It was observed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom.

(ii) The nucleus is surrounded by negatively charged electrons which are revolving around the nucleus at very high speeds in circular paths called **orbits**.

Thus, the Rutherford's model of atom resembles the solar system in which the nucleus plays the role of the sun and revolving electrons play the role of planets.

(iii) The electrons and the nucleus are held together by electrostatic forces of attraction.

(iv) Most of the space in an atom between the nucleus and the revolving electrons is empty.

CONCEPT OF ATOMIC NUMBER AND MASS NUMBER

Atomic Number

The number of unit positive charges carried by the nucleus of an atom is termed as **the atomic number.** Since the positive charge on the nucleus is due to the presence of protons in it and each proton carries one unit positive charge, therefore, the atomic number is numerically equal to the *number of protons present* in the nucleus of an atom. For example, the number of protons in the hydrogen nucleus is 1 and therefore, atomic number of hydrogen is 1.

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Moreover, the number of protons in an atom is equal to the number of electrons since atom on the whole is electrically neutral. Thus, atomic number of an element is equal to the number of protons present in the nucleus or the number of electrons present outside the nucleus. It is generally denoted by the letter Z. Thus,

Atomic number (Z) = Number of protons (p)
= Number of electrons (e)

Mass Number

Since the electrons are of negligible mass, the entire mass of the atom is due to protons and neutrons only. These particles are present in the nucleus and are collectively known as **nucleons.** *The sum of the neutrons and protons is known as* **mass number.**

Mass number =
No. of protons + No. of neutrons

Mass number is generally represented by the letter A.

Therefore, from the knowledge of atomic number and mass number of an element, the number of electrons, protons and neutrons can be easily predicted. We know

Atomic number, Z = No. of protons (p)
= No. of electrons (e)
Mass number, A = No. of protons (p) + No. of neutrons (n)

Therefore, for an atom with mass number A and atomic number Z :

Number of electrons = Z, Number of protons = Z

Number of neutrons = A – Z

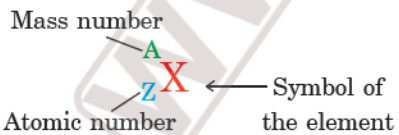
For example, lithium has an atomic number (Z) = 3 and mass number (A) = 7. Therefore,

Number of electrons = Atomic number = 3

Number of protons = Atomic number = 3

Number of neutrons = A – Z = 7 – 3 = 4

Generally, an atom is represented by its symbol for the element. Atomic number is written on the lower side of the symbol and the mass number is written on the upper side. For example, lithium with atomic number equal to 3 and mass number equal to 7 may be represented as $^{7}_{3}Li$.



NOTE

While using the notation $^{A}_{Z}X$, it is essential to know whether the species is neutral atom, a cation or an anion. If it is neutral, then number of protons = number of electrons = atomic number. If the species is an ion, determine whether the number of protons are larger (for cations) or smaller (for anions) than the number of electrons. Number of neutrons is always given by A – Z whether the species is neutral or ion.

ISOTOPES, ISOBARS AND ISOTONES

Isotopes

Atoms of the same element which have the same atomic number but different mass numbers are called ***isotopes.***

Since the atomic number of different isotopes of the same element is same, it means that **they have same number of electrons and protons.** The difference in their mass numbers is due to different number of neutrons present in their nuclei.

Hydrogen is the common example which has three isotopes. These are commonly known as *hydrogen, deuterium* and *tritium*. These three isotopes have the same atomic number, one, but different mass numbers 1, 2 and 3 respectively as given below.

Isotope	Atomic number	Mass number	No. of electrons	No. of protons	No. of neutrons
Hydrogen $^{1}_{1}H$ (or protium)	1	1	1	1	0
Deuterium $^{2}_{1}H$(or D)	1	2	1	1	1
Tritium $^{3}_{1}H$(or T)	1	3	1	1	2

Similarly, chlorine has two isotopes having same atomic number, Z = 17 whereas, their mass numbers are 35 and 37.

Isotope	Atomic number	Mass number	No. of electrons	No. of protons	No. of neutrons
$^{35}_{17}Cl$	17	35	17	17	18
$^{37}_{17}Cl$	17	37	17	17	20

Isotopes of some other elements are

Element	Isotopes
Carbon	$^{12}_{6}C$, $^{13}_{6}C$, $^{14}_{6}C$
Oxygen	$^{16}_{8}O$, $^{17}_{8}O$, $^{18}_{8}O$
Nitrogen	$^{14}_{7}N$, $^{15}_{7}N$
Sulphur	$^{32}_{16}S$, $^{33}_{16}S$, $^{34}_{16}S$, $^{36}_{16}S$
Uranium	$^{235}_{92}U$, $^{238}_{92}U$, $^{239}_{92}U$

It may be noted that the chemical properties of atoms are mainly controlled by electrons, which are determined by the number of protons in the nucleus. Therefore, ***all the isotopes of a given element will show almost same chemical properties.***

Isobars

Atoms of different elements having the same mass number but different atomic numbers are called ***isobars.***

Since isobars have same mass number, therefore, **the sum of protons and neutrons in the nucleus of each atom is the same.** These atoms differ in their

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atomic number and therefore, they have different number of protons (or electrons) and also different number of neutrons.

For example, $^{40}_{18}Ar$, $^{40}_{19}K$ and $^{40}_{20}Ca$ are isobars.

The characteristics of these isobars are:

Isobar	Atomic number	Mass number	No. of electrons	No. of protons	No. of neutrons
$^{40}_{18}Ar$	18	40	18	18	22
$^{40}_{19}K$	19	40	19	19	21
$^{40}_{20}Ca$	20	40	20	20	20

Isobars are atoms of different elements and hence they have different properties.

Isotones

Atoms having same number of neutrons but different mass numbers are called ***isotones.***

Thus, **isotones have same number of neutrons.** These atoms differ in mass number as well as atomic number. For example, $^{30}_{14}Si$ (14 protons, 16 neutrons), $^{31}_{15}P$ (15 protons, 16 neutrons) and $^{32}_{16}S$ (16 protons, 16 neutrons) are isotones because all have 16 neutrons. Similarly, $^{14}_{6}C$ (6 protons, 8 neutrons), $^{15}_{7}N$ (7 protons, 8 neutrons) and $^{16}_{8}O$ (8 protons, 8 neutrons) are isotones because all have 8 neutrons.

REMEMBER

- **Isotopes** have same number of protons but different number of neutrons.
- **Isobars** have different number of protons as well as neutrons but same sum of protons and neutrons.
- **Isotones** have same number of neutrons but different number of protons.
- In all neutral atoms, no. of electrons = no. of protons.

SOLVED EXAMPLES

Example 1.

How many protons, electrons and neutrons are there in the following nuclei ?

(i) $^{17}_{8}O$ *(ii)* $^{25}_{12}Mg$ *(iii)* $^{80}_{35}Br$

Solution: *(i)* $^{17}_{8}O$

Atomic number, Z = 8, Mass number, A = 17

No. of protons = No. of electrons = Z = 8

No. of neutrons + No. of protons = A

No. of neutrons + 8 = 17

or No. of neutrons = 17 – 8 = 9

(ii) $^{25}_{12}Mg$

Atomic number, Z = 12, Mass number, A = 25

No. of protons = No. of electrons = Z = 12

No. of neutrons = A – No. of protons

= 25 – 12 = 13.

(iii) $^{80}_{35}Br$

Atomic number, Z = 35, Mass number, A = 80

No. of protons = No. of electrons = Z = 35

No. of neutrons = A – No. of protons

= 80 – 35 = 45.

Example 2.

The number of electrons, protons and neutrons in a species are equal to 18, 16 and 16 respectively. Assign proper symbol to the species. **N.C.E.R.T.**

Solution: Atomic number is equal to number of protons = 16

So, the element is sulphur (S)

Mass number = No. of protons + No of neutrons

= 16 + 16 = 32

Species is not neutral because the number of protons is not equal to number of electrons. It is anion with charge equal to excess electrons = 18 – 16 = 2

∴ Symbol is $^{32}_{16}S^{2-}$

Example 3.

Complete the following table :

Particle	*Mass Number*	*Atomic Number*	*Protons*	*Neutrons*	*Electrons*
O		8		8	
Al	27				13
Cl^-	35		17		
Mg^{2+}				12	10

Solution: *First row :* Mass number = $n + p$

But p = At. No. = 8

n = 8

∴ Mass number = 8 + 8 = 16

Now $e = p$ = 8

Second row : Atomic number

$= p = e$ = 13

Protons = 13

$n + p$ = Mass number

= 27

n = 27 – 13 = 14

Third row : Atomic No. = p = 17

$n + p$ = Mass number

= 35

∴ n = 35 – 17 = 18

Now electrons in Cl atom = p = 17

∴ Electrons in Cl^- ion = 17 + 1 = 18

Fourth row : Mass number = $n + p$

But $p = e$ in Mg-atom

Electrons in Mg^{2+} = 10

Electrons in Mg = 10 + 2 = 12

∴ p = 12

Mass number = 12 + 12 = 24

Atomic No. = p = 12

Thus, the complete table is given below :

Particle	*Mass Number*	*Atomic Number*	*Protons*	*Neutrons*	*Electrons*
O	16	8	8	8	8
Al	27	13	13	14	13
Cl^-	35	17	17	18	18
Mg^{2+}	24	12	12	12	10

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❑ **Example 4.**

An element with mass number 81 contains 31.7% more neutrons as compared to protons. Assign the atomic symbol. **N.C.E.R.T.**

Solution: We know

Mass number = No. of protons + No. of neutrons = 81

i.e., $p + n = 81$

Let number of protons $= x$

$$\text{Number of neutrons} = x + \frac{x \times 31.7}{100}$$

$$= 1.317\,x$$

$$\therefore \quad x + 1.317x = 81$$

$$x = \frac{81}{2.317} = 34.96 = 35$$

Symbol = $^{81}_{35}\text{Br}$

❑ **Example 5.**

An ion with mass number 56 contains 3 units of positive charge and 30.4% more neutrons than electrons. Assign the symbol for the ion. **N.C.E.R.T.**

Solution: Since the ion carries 3 units of positive charge, it will have 3 electrons less than the number of protons.

Let number of electrons = x

No. of protons = $x + 3$

$$\text{No. of neutrons} = x + \frac{x \times 30.4}{100}$$

$$= x + 0.304\,x = 1.304\,x$$

Now, No. of protons + No. of neutrons = 56

$$x + 3 + 1.304\,x = 56$$

$$2.304\,x = 53$$

$$x = \frac{53}{2.304} = 23$$

No. of electrons = 23, No of protons = 23 + 3 = 26

No. of neutrons = 56 – 26 = 30

Symbol = $^{56}_{26}\text{Fe}^{3+}$

Practice Problems

1. How many protons and neutrons are present in the following nuclei ?

(*i*) $^{12}_{6}\text{C}$ (*ii*) $^{56}_{26}\text{Fe}$

(*iii*) $^{88}_{38}\text{Sr}$ (*iv*) $^{238}_{92}\text{U}$.

2. An atom having atomic mass number 13 has 7 neutrons. What is the atomic number of the atom ? *(NCERT Exemplar Problem)*

3. Are neutrons present in all atoms ?

4. What is the relationship between the following atoms of strontium ?

$^{87}_{38}\text{Sr}$ and $^{90}_{38}\text{Sr}$

5. How many electrons, protons and neutrons are present in each of the following ?

(*i*) $^{137}_{56}\text{Ba}^{2+}$ (*ii*) $^{19}_{9}\text{F}^{-}$ (*iii*) $^{226}_{88}\text{Ra}$

6. From the following nuclei select the isotopes and isobars :

$^{238}_{92}\text{U}$, $^{234}_{90}\text{Th}$, $^{234}_{92}\text{U}$, $^{234}_{91}\text{Pa}$

7. An isotope of $^{112}_{50}\text{Sn}$ contains 68 neutrons. What will be its mass number ?

8. An ion with mass number 37 possesses one unit of negative charge. If the ion contains 11.1% more neutrons than the electrons, find the symbol of the ion. **N.C.E.R.T.**

Answers to Practice Problems

1. (*i*) 6, 6 (*ii*) 26, 30 (*iii*) 38, 50 (*iv*) 92, 146

2. A = 13, A – Z = 7 ∴ Z = 6

3. No, in all atoms except hydrogen.

4. These are isotopes.

5. (*i*) 54, 56, 81 (*ii*) 10, 9, 10 (*iii*) 88, 88, 138

6. isotopes : $^{238}_{92}\text{U}$, $^{234}_{92}\text{U}$; isobars : $^{234}_{90}\text{Th}$, $^{234}_{92}\text{U}$, $^{234}_{91}\text{Pa}$

7. 118

8. $^{37}_{17}\text{Cl}^{-}$

Hints & Solutions on page 68

DRAWBACKS OF RUTHERFORD MODEL

According to Maxwell theory of electromagnetic radiation, a charged body moving under the influence of attractive forces loses energy continuously in the form of electromagnetic radiation. Thus, the electron is a charged body and it should emit radiations while revolving around the nucleus. As a result of this, the electron should lose energy at every turn and move closer and closer to the nucleus following a spiral path (Fig. 9). Consequently, the orbit will become smaller and smaller and finally the electron would fall into the nucleus. In other words, the atom should collapse. The calculations have shown that it should take only 10^{-8} s for an electron to spiral into the nucleus. However, **this never happens.**

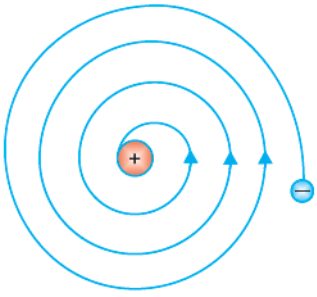

Fig. 9. Gradual decrease in the distance between the electron and the nucleus.

Therefore, **Rutherford model cannot explain the stability of an atom.**

There is another serious drawback of the Rutherford model. This model does not explain the

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structure of atoms *i.e.*, the distribution of electrons around the nucleus and their energies.

DEVELOPMENTS LEADING TO THE BOHR MODEL OF ATOM

During the period of development of new models to improve Rutherford model of an atom, two new concepts played a major role. These are :

1. **Dual behaviour of the electromagnetic radiation.** This means that light has both *particle like* and *wave like* properties.
2. **Atomic spectra.** The experimental results regarding atomic spectra of atoms can only be explained by assuming quantized (fixed) electronic energy levels in atoms.

Let us briefly learn about these concepts before studying a new model proposed by Niels Bohr known as **Bohr Model of Atom.**

NATURE OF LIGHT AND ELECTROMAGNETIC RADIATION

The earliest view of light, due to Newton, regarded light as made up of particles (commonly termed as corpuscles of light). The particle nature of light explained some of the experimental facts such as reflection and refraction of light. However, it failed to explain the phenomena of interference and diffraction. The corpuscular theory was, therefore, discarded and Huygens proposed wave like character of light. With the help of wave theory of light, Huygens explained the phenomena of interference and diffraction.

Electromagnetic Radiation

In 1870, James Clark Maxwell proposed that light and other forms of radiant energy propagate through space in the form of waves. These waves have electric and magnetic fields associated with them and are, therefore, called **electromagnetic radiations** or **electromagnetic waves.**

Wave Motion

All of us are familiar with the waves on the surface of water obtained by throwing a stone into a quiet pond. The waves originate from the centre of disturbance and propagate in the form of up and down movements. *The point of maximum upward displacement* is called **crest** while *the point of maximum downward displacement* is called **trough.** Thus, waves may be considered as ***disturbances which originate from some vibrating source and travel outwards as a continuous sequence of alternating crests and troughs.*** It is shown in Fig. 10.

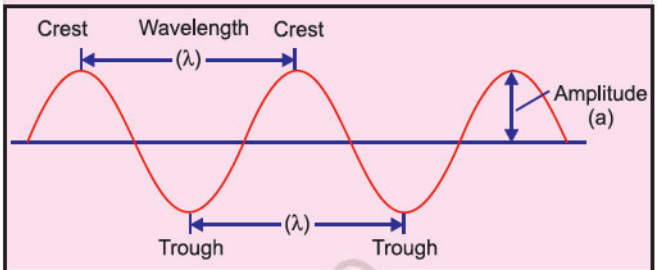

Fig. 10. Wave motion.

Characteristics of Wave Motion

All waves are characterised in terms of their wavelength, frequency, velocity and amplitude. These are discussed below :

1. Wavelength (λ, lambda)

***The distance between two adjacent crests or troughs* is called wavelength.**

It is denoted by the Greek letter *lambda* (λ) and is generally expressed in terms of Angstrom units, denoted as Å [$1Å = 10^{-8}$ cm or 10^{-10} m]. It can also be expressed as micron meter (μ), millimicron meter (mμ), nanometer (nm), pico meter (pm), etc. These units are related to SI unit metre (m) as :

$1 Å = 10^{-10}$ m ; $1 \mu = 10^{-6}$ m, $1 m\mu = 10^{-9}$ m, $1 nm = 10^{-9}$ m, $1 pm = 10^{-12}$ m

2. Frequency (ν, nu)

***The number of waves which pass through a given point in one second is* known as the frequency.**

It is denoted by the Greek letter *(ν) nu. The units of frequency are cycles per second* or simply *reciprocal of seconds* (s^{-1}). The SI unit of frequency is hertz (Hz, s^{-1}) after the name of Heinrich Hertz.

1 Hz = 1 cycle per second.

A cycle is said to be completed when a wave consisting of crest and trough passes through a point.

3. Velocity (c)

***The distance travelled by a wave in one second* is called the velocity of the wave.**

It is generally denoted by the letter *c* and is expressed as m s^{-1}.

4. Amplitude (*a*)

It is the height of crest or depth of trough of wave.

It is generally expressed by the letter '*a*'. The amplitude of the wave determines the intensity or brightness of radiation.

5. Wave number ($\bar{\nu}$, *nu bar*)

It is defined ***as the number of wavelengths per centimetre and is equal to the inverse of wavelength expressed in centimetre.***

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It is denoted by *nu bar* ($\bar{\nu}$) and is expressed in cm^{-1}. It can also be expressed as m^{-1} (S.I. units). Thus,

$$\text{Wave number} = \frac{1}{\text{Wavelength}}$$

$$\bar{\nu} = \frac{1}{\lambda}$$

Relationship between wavelength, wave number, frequency and velocity. These three characteristics are related as :

$$c = \lambda \times \nu$$

or $$\nu = \frac{c}{\lambda} \text{ and } \frac{1}{\lambda} = \bar{\nu}$$

$\therefore$ $$\nu = c\bar{\nu}$$

Characteristics of Electromagnetic Radiations

The important **characteristics** of electromagnetic radiations are :

(*i*) These consist of electric and magnetic fields that oscillate in the directions perpendicular to each other and both are perpendicular to the direction in which the wave is travelling as shown in Fig. 11. The two field components have the same wavelength and frequency.

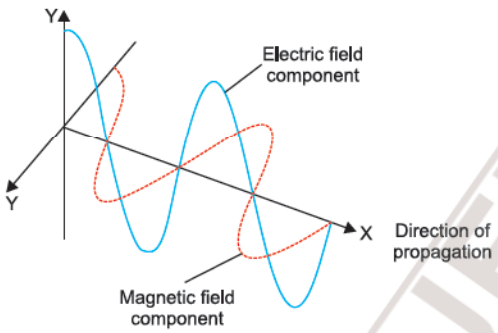

Fig. 11. Electromagnetic radiation consisting of electric and magnetic fields oscillating in planes perpendicular to each other and also perpendicular to the direction of propagation.

(*ii*) All electromagnetic waves travel with the same speed. In vacuum, the speed of all types of electromagnetic radiation is 3.00×10^8 m s^{-1} (2.997925×10^8 ms^1 to be more precise). This speed is called the speed of light.*

(*iii*) These electromagnetic radiations do not require any medium for propagation. For example, light reaches us from the sun through empty space.

Electromagnetic Spectrum

As already discussed, all electromagnetic waves have the same speed ($3{\cdot}0 \times 10^8$ m s^{-1}). However, the different types of radiations differ from one another in their wavelengths and therefore, in frequency ($\nu = \frac{c}{\lambda}$ and c is constant). Thus, the electromagnetic radiation with a long wavelength has low frequency while the radiation with short wavelength has a large frequency. The complete range of electromagnetic waves is called **electromagnetic spectrum.** Thus,

the arrangement of different types of electromagnetic radiations in the order of increasing wavelengths (or decreasing frequencies) is known as ***electromagnetic spectrum.***

The complete electromagnetic spectrum is shown in Fig. 12 below. Different regions of the spectrum are identified by different names.

It may be noted that some books include cosmic rays in graphical representation of electromagnetic spectrum. But according to research in astrophysics, cosmic rays are high energy charged particles and should not be included in electromagnetic spectrum.

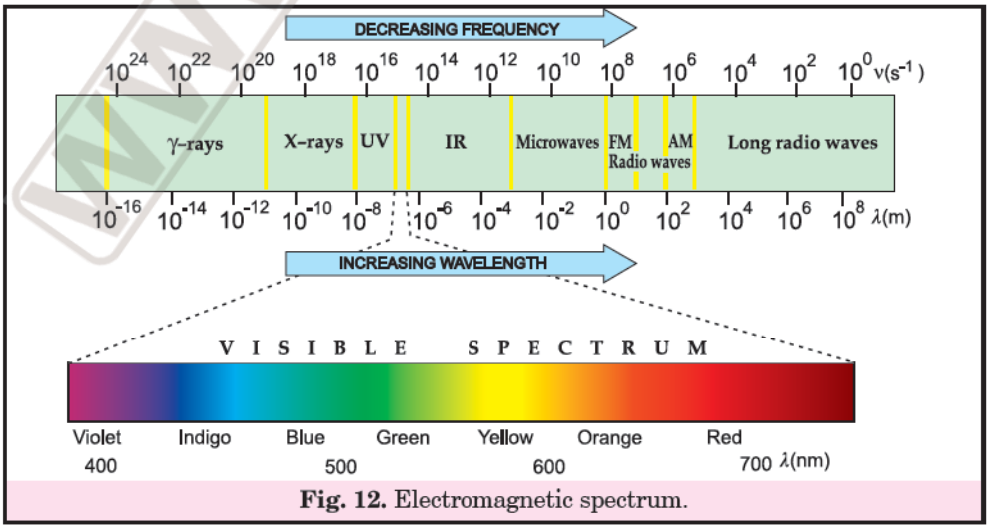

Fig. 12. Electromagnetic spectrum.

* The speed of light in air is slightly less than its speed in vacuum. However, the difference is so small that it can be ignored in most cases.

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It is interesting to note that visible light, which human eye can detect constitutes only small portion of the total electromagnetic spectrum. The visible spectrum is also shown separately. Different colours in the spectrum correspond to waves of different wavelengths and frequencies. Out of the various colours in the visible range, violet colour corresponds to radiation of maximum frequency (7.5×10^{14} Hz) and minimum wavelength (380 nm) while the red colour corresponds to the radiation of minimum frequency (4.0×10^{14} Hz) and maximum wavelength (760 nm). The frequencies and wavelengths of the radiations corresponding to colours in between lie between these two extreme values.

It is clear from Fig. 12 that radiowaves have the lowest frequencies or highest wavelengths and the gamma rays have the highest frequencies or lowest wavelengths. The different types of radiations are arranged in the ***decreasing order of frequencies*** *or* ***increasing order of wavelengths*** *as :*

Gamma rays, X-rays, ultra-violet radiations, visible radiations, infra-red radiations, microwaves and radiowaves.

SOLVED EXAMPLES

Example 6.

Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate the frequency and wave number of this light. **N.C.E.R.T.**

Solution: Wavelength of yellow light (λ) = 580 nm

$= 580 \times 10^{-9}$ m

[1 nm = 10^{-9} m]

We know that frequency (ν) is related to wavelength as:

$$\lambda \times \nu = c \text{ or } \nu = \frac{c}{\lambda}$$

where, c, velocity of light $= 3.0 \times 10^8$ m s^{-1}

$$\therefore \quad \nu = \frac{3.0 \times 10^8 \text{ m s}^{-1}}{580 \times 10^{-9} \text{ m}}$$

$$= 5.17 \times 10^{14} \text{ s}^{-1}$$

Again, wave number, $\bar{\nu} = \frac{1}{\lambda}$

$$\therefore \quad \bar{\nu} = \frac{1}{580 \times 10^{-9} \text{ m}}$$

$$= 1.72 \times 10^6 \text{ m}^{-1}$$

Therefore, frequency $= \mathbf{5.17 \times 10^{14}\ s^{-1}}$

and wave number $= \mathbf{1.72 \times 10^6\ m^{-1}}$

Example 7.

The Vividh Bharti station of All India Radio, Delhi broadcasts on a frequency of 1368 kHz. Calculate the wavelength of the electromagnetic radiation emitted by the transmitter. Which part of the electromagnetic spectrum does it belong ? **N.C.E.R.T.**

Solution: The frequency of the radiation emitted,

$$\nu = 1368 \text{ kHz} = 1368 \times 10^3 \text{ Hz}$$

$$= 1368 \times 10^3 \text{ s}^{-1}$$

We know that $\lambda \times \nu = c$ or $\lambda = \frac{c}{\nu}$

where $c = 3.0 \times 10^8$ m s^{-1}

$$\lambda = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{1368 \times 10^3 \text{ s}^{-1}} = \mathbf{219.3\ m}$$

Thus, wavelength of radiowave broadcast by the station $= \mathbf{219.3\ m.}$

It belongs to **radiowave region** of the electromagnetic spectrum.

Example 8.

The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelengths in frequencies (Hz). **N.C.E.R.T.**

Solution: Wavelength of violet light, λ = 400 nm

$= 400 \times 10^{-9}$ m

Frequency, $\nu = \frac{c}{\lambda}$

where c is speed of light = 3.0×10^8 m s^{-1}

$$\therefore \quad \nu = \frac{3.0 \times 10^8 \text{ m s}^{-1}}{400 \times 10^{-9} \text{ m}}$$

$$= \mathbf{7.5 \times 10^{14}\ Hz}$$

Wavelength of red light, λ = 750 nm

$= 750 \times 10^{-9}$ m

$\therefore$ Frequency, $\nu = \frac{c}{\lambda}$

$$= \frac{3.0 \times 10^8 \text{ m s}^{-1}}{750 \times 10^{-9} \text{ m}} = \mathbf{4.0 \times 10^{14}\ Hz}$$

Thus, the range of visible spectrum in terms of frequency is from $\mathbf{4.0 \times 10^{14}}$ Hz to $\mathbf{7.5 \times 10^{14}}$ Hz.

Practice Problems

9. The wavelength of a spectral line of cesium is 460 nm. Calculate the frequency of the line.

10. A certain radio station broadcasts on a frequency of 980 kHz (kilohertz). What is the wavelength of electromagnetic radiation broadcast by the radio station ? **N.C.E.R.T.**

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11. Calculate the wave number of radiations having a frequency of 4×10^{11} kHz.

12. The wavelength of blue light is 480 nm. Calculate the frequency and wave number of this light.

13. Calculate (*i*) wave number and (*ii*) frequency of yellow radiation having wavelength 5800 Å.

N.C.E.R.T.

14. The wavelength of a beam of light is 25.0 μm. What is its frequency and wave number ?

Answers to Practice Problems

9. $6.52 \times 10^{14}\ sec^{-1}$
10. 306 m
11. $1.33 \times 10^{6}\ m^{-1}$
12. $6.25 \times 10^{14} s^{-1}$, $2.08 \times 10^{6}\ m^{-1}$
13. (*i*) $1.724 \times 10^{6}\ m^{-1}$, (*ii*) $5.172 \times 10^{14}\ s^{-1}$
14. 1.2×10^{13}Hz, 4.0×10^{4} m

Hints & Solutions on page 68

PARTICLE NATURE OF ELECTROMAGNETIC RADIATION AND PLANCK'S QUANTUM THEORY

The electromagnetic wave theory of radiation believed in the *continuous generation of energy*. This theory explained the phenomenon of propagation of light such as diffraction* and interference* quite successfully but it failed to explain many phenomena such as *black body radiation* and *photoelectric effect*.

(*a*) Black Body Radiation

When solids are heated they emit radiations over a wide range of wavelengths. For example, when an iron bar is heated in a furnace, it emits radiation and becomes dull red and then progressively becomes more and more red as the temperature increases. When heating is continued, it becomes brighter orange, then yellow, then white and finally, it becomes blue at very high temperatures. As we know, red light has higher wavelength and blue light has lower wavelength so in terms of wavelength, the radiation emitted goes from a higher wavelength to a lower wavelength. Since the longer wavelengths (red) have lower intensity and shorter wavelengths have higher intensity, this means that if this trend were to continue, the intensity would keep on increasing indefinitely as the wavelength becomes shorter and shorter and may enter ultra violet region. However, the intensity of black body radiation does not show this expected behaviour. **An ideal body which emits and absorbs radiations of all wavelengths or frequencies** is called **black body** and the radiation emitted by this body is called **black body radiation.** It has characteristic distribution at a given temperature as shown in Fig. 13. At a given temperature, intensity of radiation emitted from a black body increases with decrease of wavelength. It reaches a maximum value at a given wavelength and then starts decreasing with further decrease of wavelength.** The figure shows the variation of intensity with wavelength at two temperatures T_1 and T_2 ($T_2 > T_1$). These results could not be explained by the classical wave theory of light. According to this theory, energy is emitted or absorbed continuously. Therefore, the energy of any electromagnetic radiation is proportional to its intensity and independent of its frequency or wavelength. Thus, the radiation emitted by the body being heated should have the same colour (wavelength or frequency) throughout, although, the intensity of the colour might change with variation in temperature.

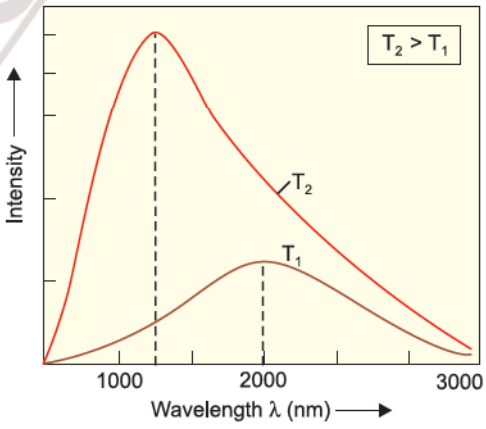

Fig. 13. Emission of radiation from a black body at different temperatures (T_2, T_1).

It is clear from the figure that at each temperature, there is a wavelength at which the intensity of radiation is maximum (λ_{max}). This maximum shifts to a lower wavelength as the temperature is increased.

(*b*) Photoelectric Effect

In 1887, H. Hertz performed very interesting experiment. He observed that when light of certain frequency strikes the surface of some metals, electrons (or electric current) are ejected from the metals.

* Diffraction is the bending of wave around an obstacle.
* Interference is the combining of two waves of the same frequency to give a wave whose disturbance at each point in space is the algebraic or vector sum of the disturbances produced by each interfering wave at that point.
** This represents variation from right to left in the Fig. 11.

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The phenomenon of ejection of electrons from the surface of a metal when light of suitable frequency strikes on it, is called **photoelectric effect.**

The emitted electrons are called **photoelectrons.**

The apparatus showing photoelectric effect is shown in Fig. 14 below. The cell consists of an evacuated chamber which contains two electrodes connected to an external circuit. The metal that exhibits the photoelectric effect is made negative electrode. When light of sufficiently high energy strikes the metal, the electrons are ejected from its surface and move towards the positive electrode and form the current flowing through the circuit.

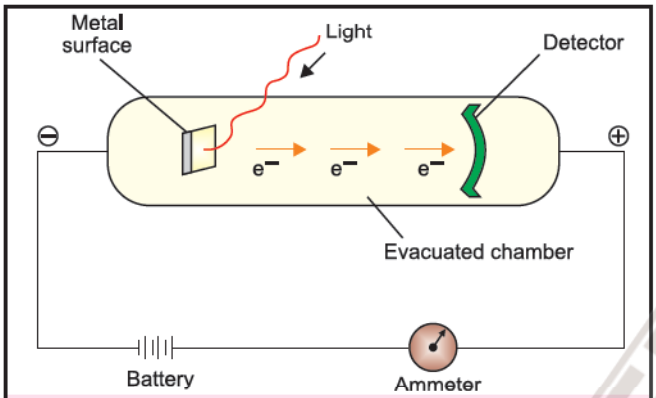

Fig. 14. Experimental device for photoelectric effect.

It may be noted that only a few metals such as **cesium, rubidium** or **potassium** in which the electrons are loosely held by the nucleus show this effect when visible light falls upon them. Experimental studies of photoelectric effect under different conditions led to the following **important observations :**

(*i*) *The electrons are ejected from the metal surface as soon as the beam of light strikes the surface i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.*

(*ii*) *For each metal, certain minimum frequency of light is needed to eject the electrons.* This is known as **threshold frequency** (ν_0) and it is different for different metals. Light of frequency less than ν_0 cannot eject electrons no matter how long it falls on the surface or how high is its intensity.

(*iii*) *The kinetic energy of the ejected electrons is directly proportional to the frequency of the incident radiation and is independent of its intensity.*

(*iv*) *The number of electrons ejected per second from the metal surface depends upon the intensity or brightness of incident radiation but does not depend upon its frequency.*

The variation of kinetic energy of photoelectrons with frequency of absorbed photons is shown below in Fig. 15 (*a*). It is clear from the figure that for ejection of electrons, the frequency (ν) of light used must be greater than threshold frequency ν_0. However, the kinetic energy remains constant with change in intensity as shown in Fig. 15 (*b*).

All these observations could not be explained on the basis of classical laws of physics. According to the classical laws of physics, the energy content of beam of light depends upon the brightness of the light. In other words, number of electrons ejected and the kinetic energy associated with them should depend on the brightness of light. However, as has been discussed above though the number of electrons ejected depends upon the brightness of light, the kinetic energy of the electrons does not. For example, red light ($\nu = 4.3 - 4.6 \times 10^{14}\ s^{-1}$) of any brightness may shine on a potassium surface for hours but it does not eject photoelectrons. But yellow light ($\nu = 5.1 - 5.2 \times 10^{14}\ s^{-1}$) of even a very weak brightness ejects photoelectrons. This is because the threshold frequency (ν_0) for potassium metal is $5.0 \times 10^{14}\ s^{-1}$ and light of frequency more than ν_0 (i.e., yellow light and not red light) can cause photoelectric effect.

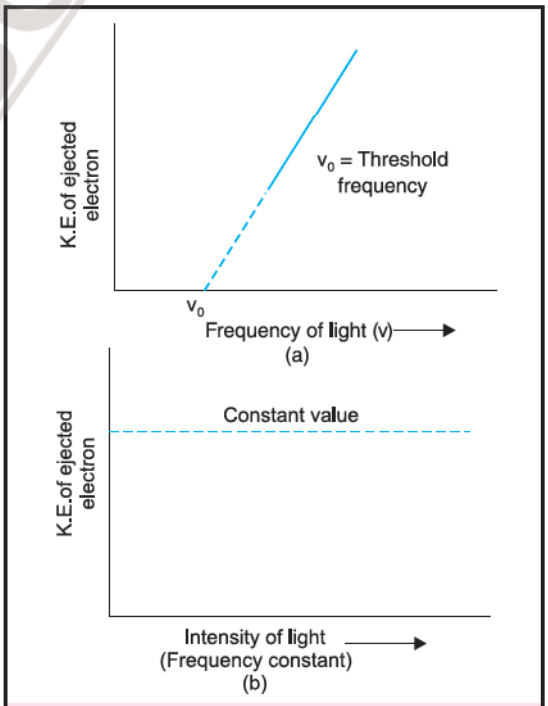

Fig. 15 Variation of kinetic energy of photoelectrons with frequency and intensity.

PLANCK'S QUANTUM THEORY OF RADIATION

All electromagnetic radiations are forms of energy. The electromagnetic wave theory believed in continuous generation of radiant energy, *i.e.*, the energy may be emitted or absorbed in any value from infinitely small to infinitely large. However, this theory could not explain the experimental results of many phenomena such as black body radiation and

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photoelectric effect. At the beginning of the twentieth century Max Planck in 1901, gave a new revolutionary theory known as **quantum theory of radiation.**

The main features of Planck's quantum theory of radiation are :

(*i*) Radiant energy is not emitted or absorbed continuously but discontinuously in the form of small packets of energy called **quanta.** Each such quantum is associated with a definite amount of energy.

In case of light, the quantum of energy is often called **photon.**

(*ii*) The amount of energy associated with a quantum of radiation is proportional to the frequency of light,

$$E \propto \nu \quad \text{or} \quad E = h\nu \qquad ...(i)$$

where the proportionality constant, *h*, is a universal constant known as **Planck's constant.** It has the value of 6.626×10^{-34} J s or 3.99×10^{-13} kJ sec mol^{-1}. This relation was found to be valid for all types of electromagnetic radiations.

(*iii*) The total amount of energy emitted or absorbed by a body will be some whole number multiple of quantum, *i.e.*,

$$E = nh\nu \quad \text{or} \quad E = \frac{nhc}{\lambda} \qquad ...(ii)$$

where *n* is an integer such as 1, 2, 3, ...

This means that a body can emit or absorb energy equal to $h\nu$, $2\ h\nu$, $3\ h\nu$.... or any other integral multiple of $h\nu$ but cannot emit or absorb energy equal to $1.6\ h\nu$, $3.2\ h\nu$ or any other fractional value of $h\nu$.

The relation [equations (*i*) and (*ii*)] give the relation between energy of the radiation and its wavelength or frequency. It shows that the higher the frequency (or the lower the wavelength), the more energetic are the corresponding photons. For example, a photon of violet light will be of more energy than that of red light because former is of larger frequency. *The concept of energy packets of light supports the corpuscular character.* It also explained the distribution of intensity in radiation from a black body as a function of frequency at different temperatures.

R.U. Curious...

❑ **When we heat an iron bar, it first becomes red, then brighter orange, yellow and finally begins to glow with white light and then blue light.**

➤ The change in colour is due to increase in frequency of radiation emitted on heating ($E = h\nu$). It becomes red in the beginning (red colour has lower frequency; low energy – low frequency) and finally blue (blue light has higher frequency; high energy – high frequency).

REMEMBER

The energy possessed by one mole of quanta (or photons) *i.e.*, Avogadro number of quanta is called **one Einstein** of energy.

1 Einstein of energy = $N_A h\nu$ or $N_A hc/\lambda$

Explanation of Photoelectric Effect using Quantum Theory

According to Einstein, when a photon strikes a metal surface, some of its energy is used up to eject the electron from the metal atom (equal to the energy binding the electron with the nucleus) and the remaining energy is given to eject electron in the form of kinetic energy. This may be expressed as :

Energy of striking photon = Binding energy + Kinetic energy of ejected electron

This means that a certain minimum amount of energy corresponding to the binding energy (also called threshold energy) is necessary to detach the electron from the metal. Thus, when a photon of energy $h\nu$, strikes a metal surface, (Fig. 16), some of its energy, called threshold energy x is used up to remove the electron from the surface and the remaining energy is imparted to the ejected electron as kinetic energy $\frac{1}{2} mv^2$. Therefore,

$$h\nu = x + \frac{1}{2} mv^2$$

If the threshold frequency is ν_0, then the threshold energy, $x = h\nu_0$ so that

$$h\nu = h\nu_0 + \frac{1}{2} mv^2$$

or $$\frac{1}{2} mv^2 = h\nu - h\nu_0$$

Therefore, the kinetic energy of ejected electron,

$$\text{K.E.} \left(\frac{1}{2} mv^2\right) = h(\nu - \nu_0)$$

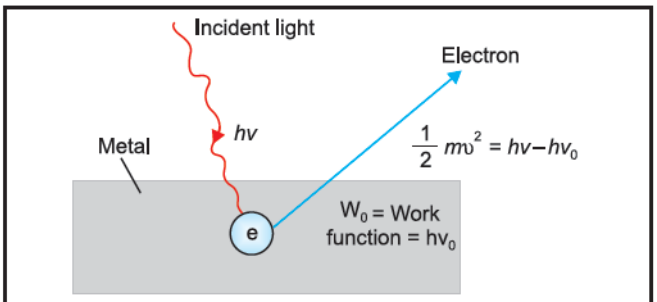

Fig. 16. Einstein's explanation for photoelectric effect.

The minimum energy required to eject the electron, ($h\nu_0$) is also called **work function, w_0.** It is characteristic of a particular metal.

The values of work function (w_0) for some common metals are given below :

Metal	Li	Na	K	Cs	Mg	Cu	Ag
w_0 (eV)	2.42	2.3	2.25	2.14	3.7	4.8	4.3

The above equation can easily explain the experimental facts as discussed ahead :

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(*i*) If the frequency of radiation ν, is less than ν_0, no electrons will be ejected whatever the intensity of radiation may be. *The threshold frequency is different for different metals.*

(*ii*) If frequency of the striking radiation is more than the threshold value (*i.e.*, $\nu > \nu_0$), the excess energy ($h\nu - h\nu_0$) is imparted to the ejected electron as kinetic energy. Thus, as the frequency of radiation increases, the kinetic energy of the electron increases.

(*iii*) Each photon can eject the electron. On increasing the intensity of light of a given frequency, the number of photons striking the surface is increased but the kinetic energy remains unchanged. Consequently, the greater intensity of light of given frequency (more than ν_0) results into more electrons being ejected but their kinetic energy does not change.

REMEMBER

The energy acquired by an electron when it is accelerated through a potential difference of 1 volt is called one electron volt (1eV)

1eV = charge on electron × 1 volt

$= 1.602 \times 10^{-19}\text{CV} = 1.602 \times 10^{-19}\text{J}$

Dual nature of Electromagnetic radiation. *Light has been regarded as waves to explain the phenomena of reflection, refraction, diffraction, etc. However, in order to explain the photoelectric effect, Einstein regarded the light as tiny particles called photons. In other words, light behaves like waves as well as like particles. Since light is a kind of radiation, it may be concluded that all radiations behave like waves as well as like particles. Such a wave like and particle like nature of radiation is known as* **dual nature of radiation.**

SOLVED EXAMPLES

Example 9.

Calculate the energy of a photon of light having frequency of $3.0 \times 10^{15}\ s^{-1}$ (Planck's constant = 6.63×10^{-34} J s).

Solution: The energy of photon is given by

$$E = h\nu$$

where frequency of the light, $\nu = 3.0 \times 10^{15}\ s^{-1}$

Planck's constant, $h = 6.63 \times 10^{-34}$ J s

$$E = (6.63 \times 10^{-34}\ \text{J s}) \times (3.0 \times 10^{15}\ s^{-1})$$

$$= 6.63 \times 3 \times 10^{-19}\ \text{J}$$

$$= \mathbf{1.99 \times 10^{-18}\ J}$$

Example 10.

Calculate and compare the energies of two radiations one with a wavelength of 800 nm and other with wavelength of 400 nm.

Solution: Energy of photon,

$$E = h\nu = \frac{hc}{\lambda}$$

Here $c = 3.0 \times 10^8\ \text{m s}^{-1}$

In first case, $\lambda = 800\ \text{nm} = 800 \times 10^{-9}\ \text{m}$

$$\therefore \quad E_1 = \frac{(6.626 \times 10^{-34}\ \text{J s}) \times (3 \times 10^8\ \text{m s}^{-1})}{800 \times 10^{-9}\ \text{m}}$$

$$= 2.48 \times 10^{19}\ \text{J}$$

In second case,

$$\lambda = 400\ \text{nm} = 400 \times 10^{-9}\ \text{m}$$

$$E_2 = \frac{(6.626 \times 10^{-34}\ \text{J s}) \times (3 \times 10^8\ \text{m s}^{-1})}{400 \times 10^{-9}\ \text{m}}$$

$$= 4.91 \times 10^{-19}\ \text{J}$$

Ratio of energy of first and second radiations,

$$\frac{E_1}{E_2} = \frac{2.48 \times 10^{-19}\ \text{J}}{4.97 \times 10^{-19}\ \text{J}} = \frac{1}{2}$$

$$\therefore \quad E_1 : E_2 = 1 : 2 \quad \text{or} \quad E_2 = 2E_1$$

Thus, energy of the radiation with wavelength 400 nm is **twice** that of the radiation of wavelength 800 nm.

Example 11.

A 100 watt bulb emits electro-magnetic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb. ***N.C.E.R.T.***

Solution: Energy emitted by the bulb = 100 watt = 100 J/s

Energy of one photon,

$$E = h\nu = \frac{hc}{\lambda}$$

$\lambda = 400\ \text{nm} = 400 \times 10^{-9}\ \text{m}$, $h = 6.62 \times 10^{-34}$ Js

$c = 3.0 \times 10^8\ \text{m s}^{-1}$

$$\therefore \quad E = \frac{(6.62 \times 10^{-34}\text{Js}) \times (3.0 \times 10^8 \text{ms}^{-1})}{400 \times 10^{-9}\text{m}}$$

$$= 4.965 \times 10^{-19}\ \text{J}$$

No. of photons emitted per sec

$$= \frac{100}{4.965 \times 10^{-19}}$$

$$= \mathbf{2.01 \times 10^{20}}$$

Example 12.

Calculate the energy of one mole of photons of radiation whose frequency is 5×10^{14} Hz. ***N.C.E.R.T.***

Solution: Frequency,

$$\nu = 5 \times 10^{14}\ s^{-1}$$

Energy of 1 photon,

$$E = h\nu$$

$$h = 6.626 \times 10^{-34}\ \text{J s}$$

$$\therefore \quad E = (6.626 \times 10^{-34}\ \text{J s}) \times (5 \times 10^{14}\ s^{-1})$$

$$= 3.313 \times 10^{-19}\ \text{J}$$

Energy of 1 mol of photons

$$= 3.313 \times 10^{-19} \times 6.022 \times 10^{23} = 199.51 \times 10^3\ \text{J mol}^{-1}$$

or $= \mathbf{199.51\ kJ\ mol^{-1}}$

Example 13.

Calculate the minimum amount of energy that the photons must possess to eject electrons from cesium metal. The threshold frequency of cesium metal is $4.6 \times 10^{14}\ s^{-1}$ ($h = 6.63 \times 10^{-34}$ J s).

Solution : [Threshold frequency (ν_0) is the minimum frequency that the photons must possess to eject electrons from metals. Therefore, the energy corresponding to ν_0 is the minimum energy required, also called work function].

Threshold frequency, $\nu_0 = 4.6 \times 10^{14}\ s^{-1}$

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Minimum energy required to eject the electrons from cesium metal,

$$E_0 = h\nu_0$$
$$h = 6.63 \times 10^{-34}\ J\ s$$
$$\therefore \quad E_0 = (6.63 \times 10^{-34}\ J\ s) \times (4.6 \times 10^{14}\ s^{-1})$$
$$= 6.63 \times 4.6 \times 10^{-20}\ J = \mathbf{3.05 \times 10^{-19}\ J}$$

❑ Example 14.

Calculate the kinetic energy of the ejected electron when ultra-violet radiation of frequency 1.6 × 10^{15} s^{-1} strikes the surface of potassium metal. Threshold frequency of potassium is 5 × 10^{14} s^{-1} ($h = 6.63 \times 10^{-34}$ J s).

Solution : K.E. of the ejected electron is given by

$$\text{K.E.} = h\nu - h\nu_0 = h(\nu - \nu_0)$$
$$\nu = 1.6 \times 10^{15}\ s^{-1},\ \nu_0 = 5 \times 10^{14}\ s^{-1}$$
$$\therefore \quad \text{K.E.} = (6.63 \times 10^{-34}\ J\ s) \times (1.6 \times 10^{15} - 5 \times 10^{14})\ s^{-1}$$
$$= (6.63 \times 10^{-34}\ J\ s) \times (11 \times 10^{14}\ s^{-1})$$
$$= \mathbf{7.29 \times 10^{-19}\ J}$$

❑ Example 15.

When light of wavelength 470 nm falls on the surface of potassium metal, electrons are emitted with a velocity of 6.4 × 10^4 m s^{-1}. What is the minimum energy required per mole to remove an electron from potassium metal ?

Solution : Velocity of emitted electrons

$$= 6.4 \times 10^4\ m\ s^{-1}$$

Kinetic energy of emitted electrons K.E. $= \frac{1}{2}mv^2$

$$= \frac{1}{2} \times 9.1 \times 10^{-31} \times (6.4 \times 10^4)^2$$
$$\therefore \quad = 1.864 \times 10^{-21}\ kg\ m^2\ s^{-2}$$
$$= 1.864 \times 10^{-21}\ J$$

Energy of photon,

$$E = h\nu = \frac{hc}{\lambda}$$
$$E = \frac{6.63 \times 10^{-34} \times 3.0 \times 10^8}{470 \times 10^{-9}}$$
$$= 4.23 \times 10^{-19}\ J$$

Minimum energy required to remove an electron = $h\nu_0$

Now, $\text{K.E.} = h\nu - h\nu_0$

or $h\nu_0 = h\nu - \text{K.E.}$

$$= 4.23 \times 10^{-19} - 1.864 \times 10^{-21}$$
$$= 421.14 \times 10^{-21}\ J$$

Minimum energy required per mole

$$= 421.14 \times 10^{-21} \times 6.023 \times 10^{23}$$
$$= 253.6 \times 10^3\ J\ mol^{-1}$$

or $= \mathbf{253.6\ kJ\ mol^{-1}}$

❑ Example 16.

When electromagnetic radiation of wavelength 300 nm strikes a metal surface of sodium, electrons are emitted with a kinetic energy of 1.68 × 10^5 J mol^{-1}. What is the minimum energy needed to remove an electron from sodium ? What is the maximum wavelength that will cause a photoelectron to be emitted ? **N.C.E.R.T.**

Solution : Energy of the striking photon,

$$E = h\nu = \frac{hc}{\lambda}$$

$h = 6.626 \times 10^{-34}$ J s, $c = 3.0 \times 10^8$ m s^{-1},

$\lambda = 300$ nm $= 300 \times 10^{-9}$ m

$$\therefore \quad E = \frac{6.626 \times 10^{-34}\ J\ s \times 3.0 \times 10^8\ m\ s^{-1}}{300 \times 10^{-9}\ m}$$
$$= 6.626 \times 10^{-19}\ J$$

Kinetic energy of emitted electrons = 1.68×10^5 J mol^{-1}

$$\text{Kinetic energy of emitted one electron} = \frac{1.68 \times 10^5}{6.022 \times 10^{23}}$$
$$= 2.79 \times 10^{-19}\ J$$

Now,

Energy of striking photon = Minimum energy required to eject electron + Kinetic energy of electron or Minimum energy required for ejection of an electron

$$= 6.626 \times 10^{-19}\ J - 2.79 \times 10^{-19}\ J$$
$$= \mathbf{3.84 \times 10^{-19}\ J}$$

The wavelength which will cause photoelectron emission,

$$\lambda = \frac{hc}{E}$$
$$= \frac{6.626 \times 10^{-34}\ J\ s \times 3.0 \times 10^8\ m\ s^{-1}}{3.84 \times 10^{-19} J}$$
$$= 5.17 \times 10^{-7}\ m$$

or $= 517 \times 10^{-9}\ m = \mathbf{517\ nm}$.

Practice Problems

15. Find energy of each of photons which
(i) have wavelength of 0.50 Å
(ii) correspond to light of frequency 3×10^{15} Hz.

16. Calculate the energy of one of the photons of a beam of light having wavelength 25.0 μm.

17. How many photons of light having a wavelength 400 nm are necessary to provide 1 J of energy ?

18. A photochemical reaction requires 9.6×10^{-16} J energy per molecule. Calculate the number of photons per molecule of light with wavelength 250 nm that is just sufficient to initiate the reaction.

19. The threshold frequency for a metal 'X' is 7.0×10^{14} s^{-1}. Calculate the kinetic energy of an electron emitted when radiation of frequency 1.0×10^{15} s^{-1} strikes the metal. **N.C.E.R.T.**

20. Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800Å. Calculate threshold frequency (ν_0) and work function (w_0) of the metal.

Answers to Practice Problems

15. *(i)* 3.98×10^{-15} J *(ii)* 1.98×10^{-18} J
16. 7.96×10^{-21} J
17. 2.01×10^{18} photons
18. 121 photons
19. 1.99×10^{-19} J
20. $4.41 \times 10^{14}\ s^{-1}$, 2.92×10^{-19} J

Hints & Solutions on page 68

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ATOMIC SPECTRA

When a beam of light from sun is passed through a prism, it splits into a series of colour bands known as *rainbow of colours :* violet, indigo, blue, green, yellow, orange and red (remembered as VIBGYOR). A similar spectrum is produced when a rainbow forms in the sky. This means that sunlight is composed of collection of electromagnetic waves having different wavelengths. The prism bends the light of different wavelengths to different extents. The red colour with the longest wavelength is deviated the least while the violet colour with the shortest wavelength is deviated the most. The splitting of light into series of colour bands is known as *dispersion* and *the series of colour bands* is called a **spectrum.** In this spectrum, there is continuity of colours *i.e.,* one colour merges into the other without any gap or discontinuity and such a spectrum is known as **continuous spectrum.**

Atomic Spectra

Unlike the spectrum obtained by analysing the sunlight, the spectra of atoms are not continuous. The spectra of atoms consist of sharp well-defined lines or bands corresponding to definite frequencies. There are two types of atomic spectra :

(i) Emission spectra

(ii) Absorption spectra.

(*i*) Emission spectra.

Emission spectra are obtained when the radiations emitted from substances that have absorbed energy (either by passing electric discharge through a gas at low pressure or by heating the substance to high temperature) are analysed with the help of spectroscope. Atoms, molecules or ions that have absorbed radiations are said to be excited. For example, when the gases or vapour of chemical substances are heated by electric spark, light is emitted. The colour of the light depends upon the substance under investigation. For example, sodium or salt of sodium gives off yellow light while potassium or salt of potassium produces a violet colour. When the radiations emitted by different substances are analysed, the spectrum obtained consists of sharp well-defined lines each corresponding to a definite frequency (or wavelength).

The emission spectrum obtained by analysing the radiation emitted by passing electric discharge through hydrogen gas at low pressure is shown in Fig. 17.

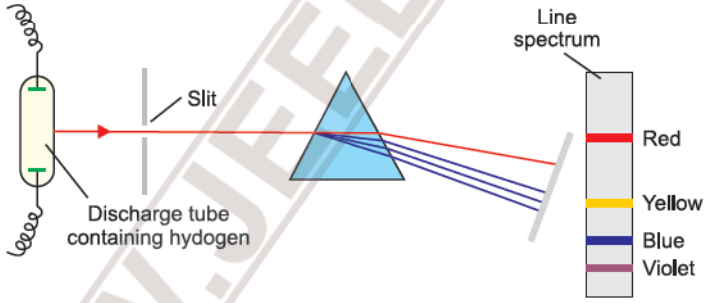

Fig. 17. The emission spectrum of hydrogen atom.

Such a spectrum consisting of lines of definite frequencies is called **line spectrum** or **discontinuous spectrum.**

The line spectrum is also known as **atomic spectrum.** The pattern of lines in the spectrum of an element is characteristic of that element, and is different from those of all other elements. In other words, *each element gives a unique spectrum irrespective of even the form in which it is present.* For example, we always get two important lines at 589 nm and 589.6 nm in the spectrum of sodium whatever may be its source. It is for this reason that *the line spectra are also regarded as the* **finger prints of atoms.**

(*ii*) Absorption spectra

When a continuous electromagnetic radiation (say white light) is allowed to pass through a gas or a solution of some salt and the transmitted light is analysed, we obtain a spectrum in which dark lines are observed in an otherwise continuous spectrum. These dark lines indicate that the radiations of corresponding wavelengths have been absorbed by the substance from the white light (Fig. 18 ahead). *Such a spectrum containing a few dark lines due to absorption of light* is known as **absorption spectrum.**

The dark lines of definite wavelengths are also characteristic of the substance. It may be noted that these dark lines appear exactly at the same place where the lines in the emission spectrum appear. For example, the emission spectrum of sodium consists of two important yellow lines at 589 and 589.6 nm. On the other hand, when white light is passed through vapour of sodium, we get dark lines in the absorption spectrum at 589 and 589.6 nm.

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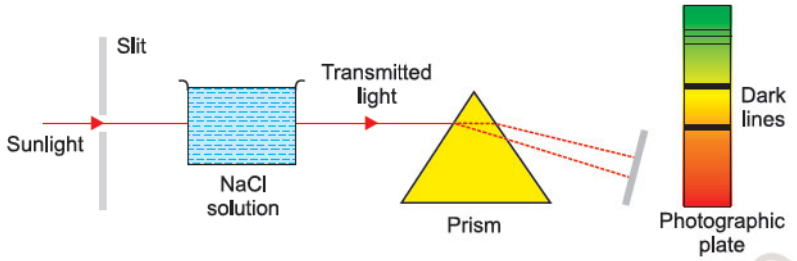

Fig. 18. Absorption spectrum of sodium chloride.

Differences between Emission and Absorption Spectra

The essential differences between emission and absorption spectra are given below :

Emission spectrum	Absorption spectrum
1. Emission spectrum is obtained when radiations emitted by the excited substance are analysed with a spectroscope.	1. Absorption spectrum is obtained when the white light is first passed through the substance (in gaseous state or in solution) and the transmitted light is analysed with a spectroscope.
2. Emission spectrum consists of bright coloured lines separated by dark spaces.	2. Absorption spectrum consists of dark lines in an otherwise continuous spectrum.

Emission Spectrum of Hydrogen Atom

The spectrum of hydrogen atom can be obtained by passing an electric discharge through the gas taken in the discharge tube under low pressure. The emitted light is analysed with the help of **spectroscope.** The spectrum consists of a large number of lines appearing in different regions of wavelengths. Some of the lines are present in the visible region while others in ultra-violet and infra-red regions.

In 1885, J.J. Balmer developed a simple relationship among the different wavelengths of the series of visible lines in the hydrogen spectrum. The relationship is :

$$\frac{1}{\lambda} = \bar{\nu}\ (\text{cm}^{-1}) = 109677\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

n is an integer equal to or greater than 3 (*i.e.*, n = 3, 4, 5 ...). It is known as **Balmer formula**.

The Balmer formula gives only the spectral lines in the visible region. These series of lines which appear in visible region were named *Balmer series.*

Soon afterwards, a series of spectral lines of hydrogen atom in different regions were discovered. These lines in different regions were grouped into five different series of lines, each being named after the name of its discoverer. These are *Lyman series, Balmer series, Paschen series, Brackett series* and *Pfund series.* Lyman series appears in the ultra-violet region. Balmer series appears in visible region while the other three series lie in the infra-red region.

Rydberg Equation

As the other series of hydrogen spectral lines were discovered, a more general expression was found as :

$$\frac{1}{\lambda} = \bar{\nu}\ (\text{in cm}^{-1}) = \text{R}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where n_1 and n_2 are integers, such that $n_2 > n_1$. R is a constant, now called the **Rydberg constant.** The value of R is **109677 cm^{-1}.** The expression is found to be valid for all the lines in the hydrogen spectrum and is also known as **Rydberg equation.**

Limiting line. The limiting line of any spectral series in the hydrogen spectrum is the line when n_2 in the Rydberg equation is infinity *i.e.*, $n_2 = \infty$. This line will have the *shortest wavelength and largest wave number.*

The complete spectrum of hydrogen atom is shown in Fig. 19.

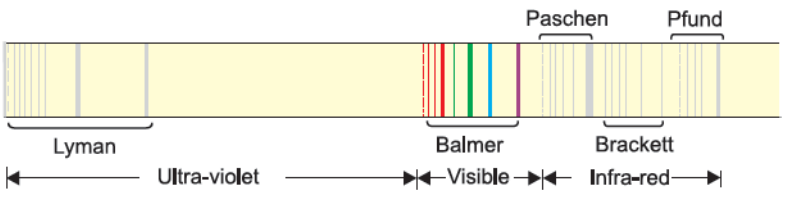

Fig. 19. Spectrum of hydrogen atom.

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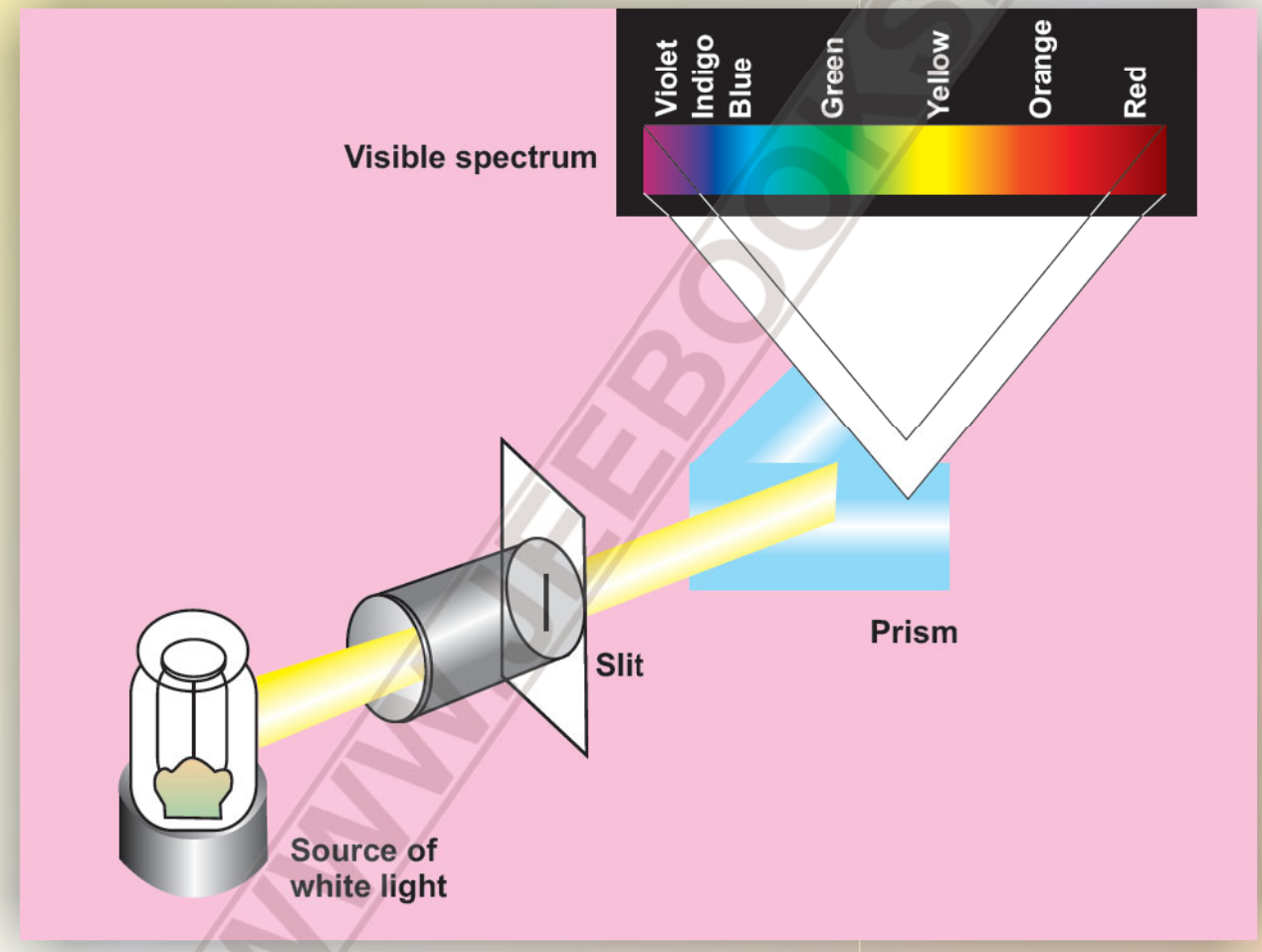
CLOSER LOOK OF ATOMIC SPECTRUM

Continuous emission spectrum of white light



Continuous emission spectrum of white light/sun

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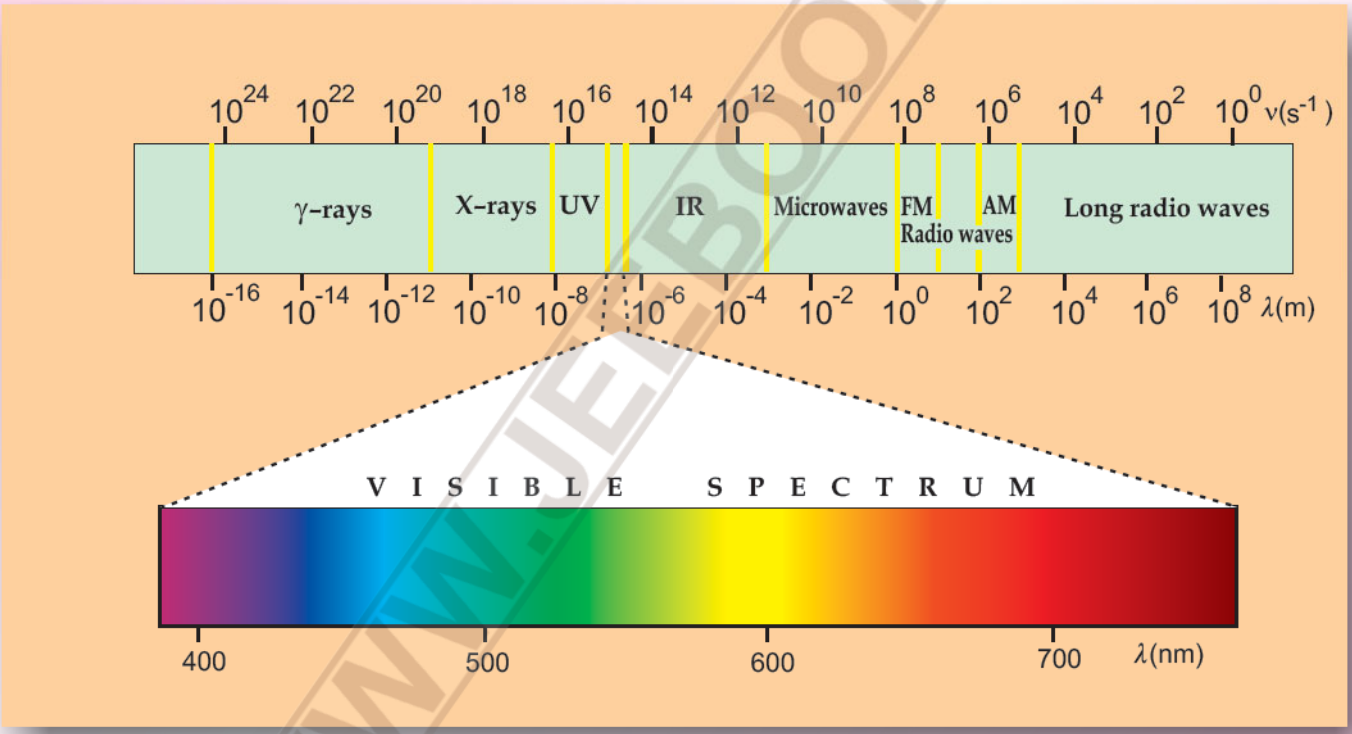
Electromagnetic spectrum



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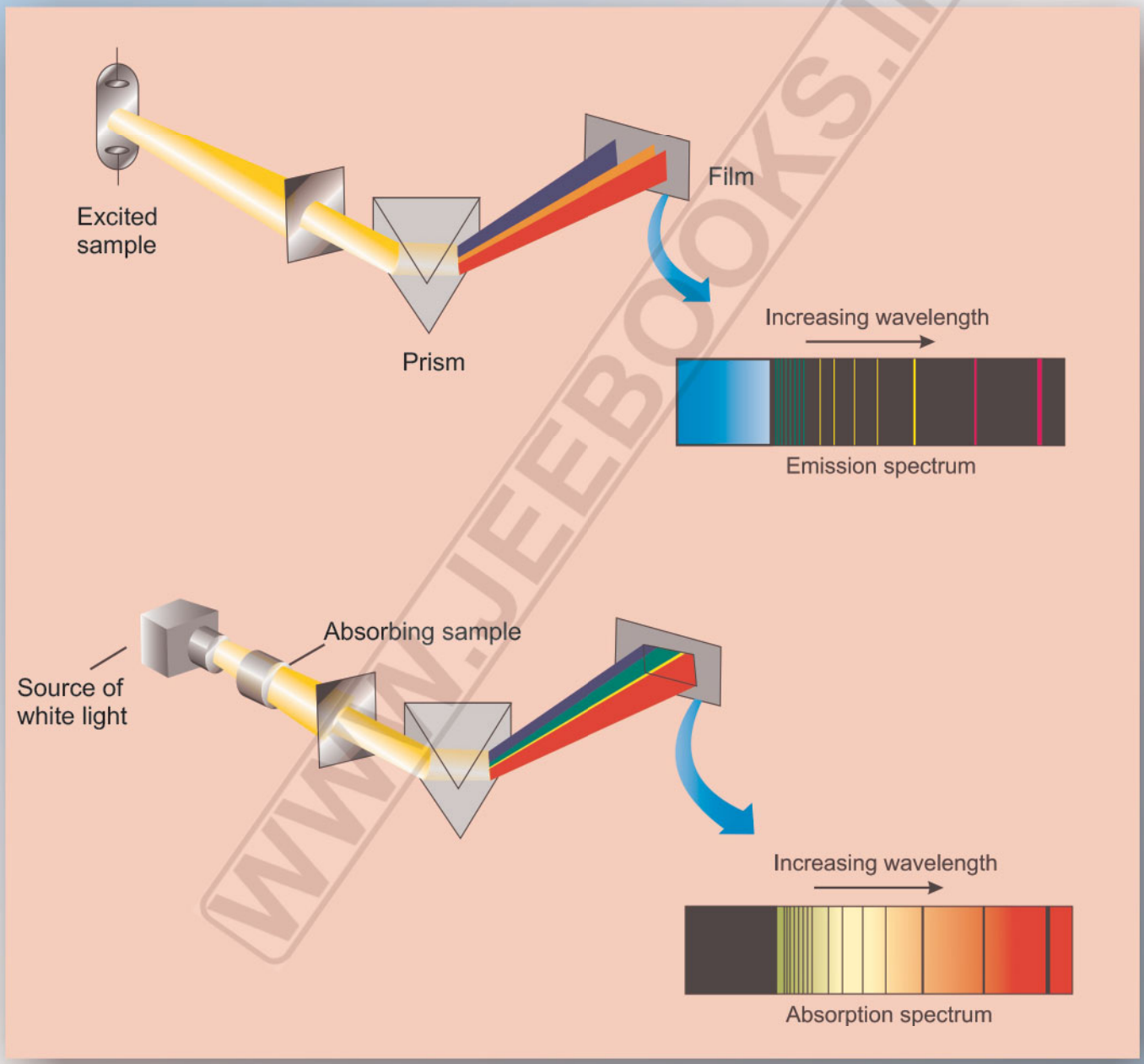
Emission and absorption spectra



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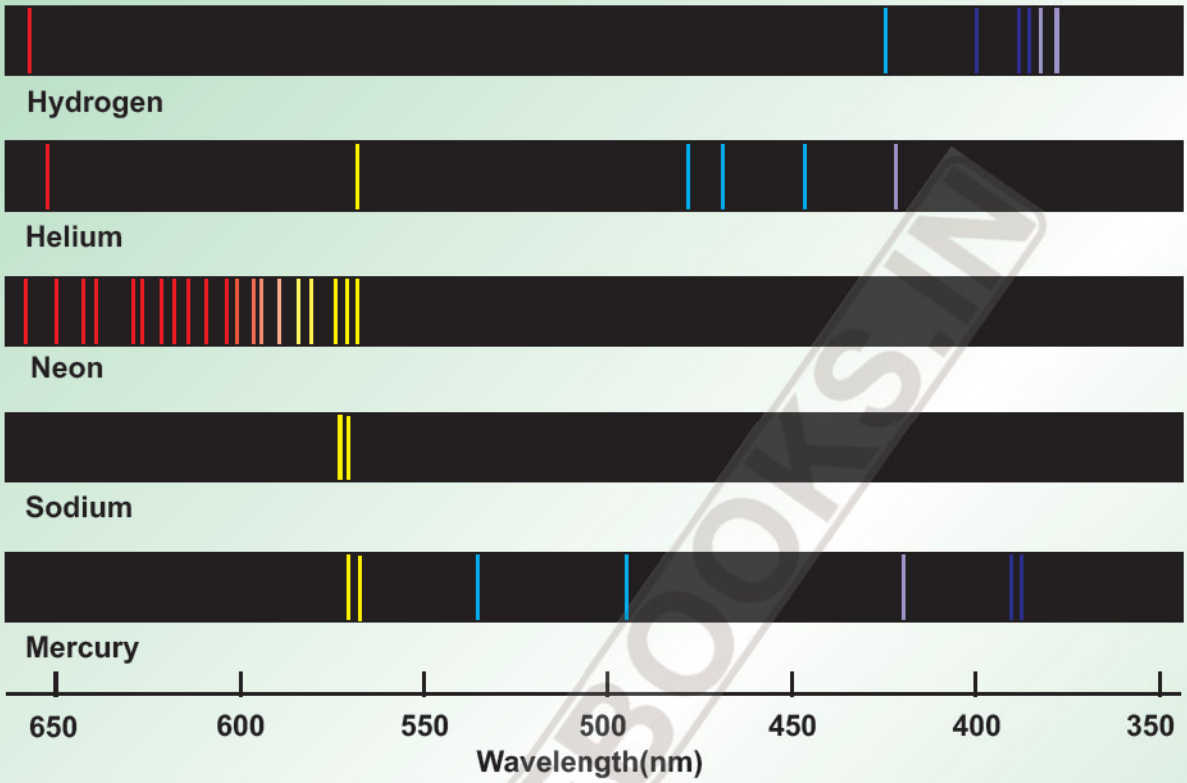
Emission spectra of some elements

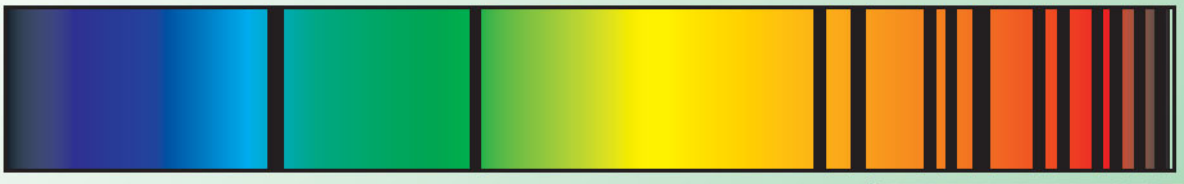


Illustrating emission and absorption spectra

It may be noted that the dark lines in absorption spectra appear exactly at the same place where the coloured lines appear in the emission spectrum.

Emission Spectrum of Barium

Absorption Spectrum of Barium



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For a given spectral series, n_1 remains constant while n_2 varies as $n_1 + 1$, $n_1 + 2$, $n_1 + 3$ .... from line to line in the same series. For example, for Lyman series $n_1 = 1$ and $n_2 = 2, 3, 4, 5$ ... and for Balmer series $n_1 = 2$ and $n_2 = 3, 4, 5$ ... All the five series, the regions in which lines appear and the values of n_1 and n_2 are given in Table 2.

Table 2. Different spectral lines in the spectrum of hydrogen atom.

Series	Region	n_1	n_2
Lyman	Ultra-violet	1	2, 3, 4, 5...
Balmer	Visible	2	3, 4, 5, 6 ...
Paschen	Infra-red	3	4, 5, 6, 7 ...
Brackett	Infra-red	4	5, 6, 7, 8 ...
Pfund	Infra-red	5	6, 7, 8, 9 ...

It may be noted that the above equation is true only for the spectral lines of hydrogen atom or hydrogen like ions. Hydrogen like ions are those which contain only one electron. For example, He^+, Li^{2+}, etc. The **Rydberg equation** for hydrogen like ions may be expressed as :

$$\frac{1}{\lambda} = \bar{\nu}\ (\text{cm}^{-1}) = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)Z^2$$

where Z is the nuclear charge, which is equal to atomic number and R is Rydberg constant. For example, for He^+, Z = 2, for Li^{2+}, Z = 3 and so on.

SOLVED EXAMPLES

Example 17.

What is the wavelength of light emitted when the electron in hydrogen atom undergoes transition from an energy level with n = 4 to an energy level with n = 2 ? What is the colour of the radiation ?

N.C.E.R.T.

Solution: According to Rydberg equation,

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Here $n_1 = 2$, $n_2 = 4$ and $R = 109677\ \text{cm}^{-1}$

$$\frac{1}{\lambda} = 109677\left(\frac{1}{2^2} - \frac{1}{4^2}\right)\ \text{cm}^{-1}$$

$$= 109677\left(\frac{1}{4} - \frac{1}{16}\right)\ \text{cm}^{-1}$$

$$= 109677 \times \frac{12}{64}\ \text{cm}^{-1}$$

or $$\lambda = \frac{64}{109677 \times 12}\ \text{cm} = 4.86 \times 10^{-5}\ \text{cm}$$

or $$\lambda = 486 \times 10^{-9}\ \text{m} = \mathbf{486\ nm}$$

This line corresponds to **bluish green colour.**

Example 18.

In the Rydberg equation, a spectral line corresponds to $n_1 = 3$ and $n_2 = 5$.

(i) Calculate the wavelength and frequency of this spectral line.

(ii) To which spectral series does this line belong?

(iii) In which region of the electromagnetic spectrum, will this line fall ?

Solution: (*i*) According to Rydberg equation,

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where $R = 109677\ \text{cm}^{-1}$, $n_1 = 3$ and $n_2 = 5$

Substituting the values,

$$\frac{1}{\lambda} = 109677\left(\frac{1}{3^2} - \frac{1}{5^2}\right)\ \text{cm}^{-1}$$

$$= 109677\left(\frac{1}{9} - \frac{1}{25}\right)\ \text{cm}^{-1}$$

or $$= 109677 \times \frac{16}{225}\ \text{cm}^{-1}$$

$\therefore$ $$\lambda = \frac{225}{109677 \times 16}\ \text{cm}$$

$$= 12.82 \times 10^{-5}\ \text{cm} = 1282 \times 10^{-9}\ \text{m}$$

or $\lambda = \mathbf{1282\ nm}$

Now $\lambda \times \nu = c$ or $\nu = \frac{c}{\lambda}$

where $c = 3.0 \times 10^8\ \text{m s}^{-1}$, $\lambda = 1282\ \text{nm} = 1282 \times 10^{-9}\ \text{m}$

$$\nu = \frac{3.0 \times 10^8\ \text{m s}^{-1}}{1282 \times 10^{-9}\ \text{m}} = \frac{3}{1282} \times 10^{17}\ \text{s}^{-1}$$

$$= \mathbf{2.34 \times 10^{14}\ s^{-1}}$$

(*ii*) Since this line corresponds to $n_2 = 3$, it belongs to **Paschen series.**

(*iii*) The spectral line will fall in **infra-red region.**

Example 19.

The wavelength of first spectral line in the Balmer series is 6561 Å. Calculate the wavelength of the second spectral line in Balmer series.

Solution: According to Rydberg equation,

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For first line in Balmer series, $n_1 = 2$, $n_2 = 3$

$\therefore$ $$\frac{1}{6561} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = R\left(\frac{5}{36}\right) \quad ...(i)$$

For second line in Balmer series, $n_1 = 2$, $n_2 = 4$

$\therefore$ $$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = R\left(\frac{3}{16}\right) \quad ...(ii)$$

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Dividing eq. (*i*) by (*ii*),

$$\frac{\lambda}{6561} = \frac{5}{36} \times \frac{16}{3}$$

$$\therefore \quad = \frac{6561 \times 5 \times 16}{36 \times 3} = 4860 \text{ Å}$$

Practice Problems

21. The first line in Balmer series corresponds to $n_1 = 2$ and $n_2 = 3$ and the limiting line corresponds to $n_1 = 2$ and $n_2 = \infty$. Calculate the wavelengths of the first and limiting lines in Balmer series.

22. Calculate the wavelength of spectral line in Lyman series corresponding to $n_2 = 3$.

23. Calculate the wavelength and energy of radiation emitted for the electronic transition from infinity (∞) to the stationary state of the hydrogen atom.

24. Calculate the wave number for the longest wavelength transition in the Balmer series of atomic hydrogen. ***N.C.E.R.T.***

Answers to Practice Problems

21. First line = 656 nm, limiting line = 364.7 nm.
22. For Lyman series $n_1 = 1$; $\lambda = 102.6$ nm.
23. $\lambda = 9.11 \times 10^{-8}$ m, $E = 2.18 \times 10^{-18}$ J
24. $1.523 \times 10^{6}\ m^{-1}$

Hints & Solutions on page 68

BOHR'S MODEL FOR HYDROGEN ATOM

To overcome the drawbacks of Rutherford's model of an atom and to explain the line spectrum of hydrogen, Niels Bohr, a Danish physicist, in 1913 proposed a model of the atom which was based upon the Planck's quantum theory of radiation. The new model is called Bohr's model of atom.

Postulates of Bohr's Model of the Atom

The basic **postulates** of Bohr's theory are :

1. *An atom consists of a small heavy positively charged nucleus in the centre surrounded by electrons. The electrons in an atom revolve around the nucleus only in certain selected circular paths which have a fixed value of radius and energy.* These paths are called **orbits.** These orbits are associated with definite energies and are called **energy shells** or **energy levels.** These are numbered as 1, 2, 3, 4 ... etc. (from the nucleus) or alternatively these are designated as K, L, M, N ... etc. shells (Fig. 20).

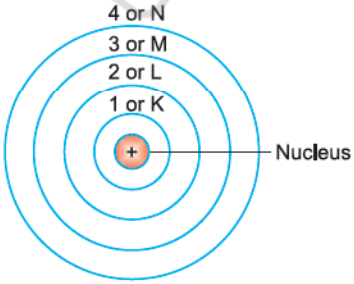

Fig. 20. Circular orbits or energy levels in an atom.

2. The energy of an electron in the orbit does not change with time. In other words, as *long as the electron remains in a particular orbit, it does not lose or gain energy.* This means that the energy of the electron in a particular energy shell remains constant. Therefore, these orbits are also called **stationary states** or **allowed energy states.** The term stationary does not mean that electron is stationary but it means that the energy of the electron does not change with time. This accounts for the stability of an atom.

3. *Only those orbits are permitted in which the angular momentum of the electron is a whole number multiple of* $\frac{h}{2\pi}$ (where h is Planck's constant). An electron, like any other moving body moving in a circular orbit has an angular momentum equal to mvr, where m is the mass of the electron moving with the velocity v and r is the radius of the orbit. Thus, according to Bohr, the angular momentum mvr is a whole number multiple of $\frac{h}{2\pi}$.

i.e., $$mvr = n\frac{h}{2\pi}$$

where $n = 1, 2, 3$ .....

In other words, angular momentum of the electron may be

$$\frac{h}{2\pi}\ (n = 1),\ \frac{h}{\pi}\ (n = 2),\ \frac{3h}{2\pi}\ (n = 3) \text{ .... etc.}$$

This postulate, therefore, introduces the concept of **quantization of angular momentum.**

4. *The energy is emitted or absorbed only when the electrons jump from one energy level to another.* When energy is supplied to an atom, its electrons absorb one or more quantum of energy and jump to higher energy levels [Fig. 21 (*a*)].

This higher energy state of electron is called its **excited state.** For example, as shown in Fig. 21 (*a*), when the electron absorbs energy equal to $E_2 - E_1$, it jumps to higher energy level. When the electron jumps back to the lower energy level, it radiates the same amount of energy [Fig. 21(*b*)]. This amount of energy emitted or absorbed is given by the difference of the energies of the two energy levels concerned. That is,

$$\Delta E = E_2 - E_1$$

where E_1 *and* E_2 *are the energies of two energy levels and* ΔE *is the difference in energies of two levels.* This means that emission and absorption of energy occur only in discrete value (equal to difference in two energy levels). In other words, the energy of the electron cannot change gradually and continuously but changes abruptly as the electron jumps from one energy level to another and not in any value. *This explains the fact that atomic spectra are discontinuous.*

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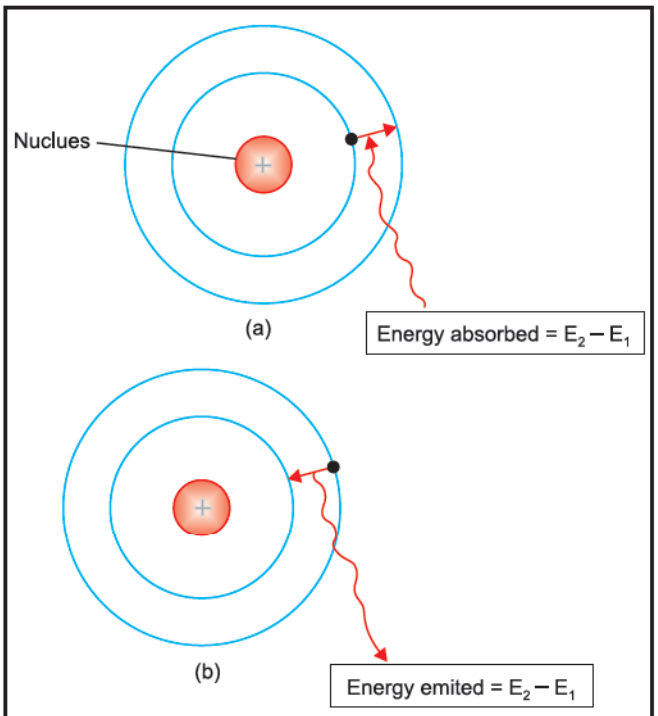

Fig. 21. Energy changes in an electron jump.

Angular momentum

As we know a linear momentum is the product of mass (m) and linear velocity (v) of the body. Similarly, angular momentum is the product of moment of inertia (I) and angular velocity (ω).

For an electron of mass m, moving in a circular path of radius r around the nucleus,

angular momentum = I × ω

Since I = mr^2 and $\omega = v/r$ where v is the linear velocity.

$$\therefore \text{ Angular momentum} = mr^2 \times \frac{v}{r} = mvr$$

Successes of Bohr's Model

The main successes of Bohr's model are :

1. Bohr's atomic model explained the stability of an atom. According to Bohr, an electron revolving in a particular orbit cannot lose energy. Therefore, emission of radiation is not possible as long as the electron remains in one of its energy levels and hence there is no cause of instability in his model.

2. Bohr's concept of atom explained successfully the atomic spectrum of hydrogen atom. From the Bohr's atomic model, it is clear that electron can have only certain definite energy levels. When the electron is present as close to the nucleus as possible, the atom has the minimum possible energy and is said to be in the **ground state.** For example, in case of hydrogen atom there is only one electron and this should be present in the lowest energy shell *i.e.*, in n = 1 shell. This represents the ground state for hydrogen atom.

When energy from some outside source is supplied to it, it can absorb a definite amount of energy and jumps to higher energy state. *Such a state of an atom in which the atom possesses more energy than possessed in the ground state is called the* **excited state.** Thus, for H-atom, first energy level (n = 1) is called the **ground state** and the higher energy levels (n = 2 first excited state, n = 3 second excited state and so on...) are called **excited states**.

This excited state is unstable and the electron tends to come back to lower energy level. This transition (change) from upper to lower level occurs with a jump and energy is emitted in the form of a quantum equal to difference in energies between the two levels. When this quantum of energy strikes the photographic plate *it gives its impression in the form of line.* For example, if the electron comes back from energy level having energy E_2 to energy level having energy E_1, then the difference ($E_2 - E_1$) may be expressed in terms of energy of photon as :

$$E_2 - E_1 = h\nu$$

Therefore, the frequency of the emitted radiation is given by

$$\nu = \frac{E_2 - E_1}{h}$$

Since E_2 and E_1 can have only definite values for an atom therefore, ν will also have only fixed values (depending upon energies of E_2 and E_1). Moreover, the energies of different energy levels are characteristic of an atom, therefore, the emitted frequencies will also be characteristic of that atom.

Now, frequency is related to wavelength as :

$$\nu = \frac{c}{\lambda} \qquad (\because v \times \lambda = c)$$

where c is the velocity of light.

$$\text{Thus,} \quad \frac{c}{\lambda} = \frac{E_2 - E_1}{h} \quad \text{or} \quad \lambda = \frac{hc}{E_2 - E_1}$$

Since h and c are constants and $E_2 - E_1$ corresponds to definite energy, thus, each transition from one level to another will produce a **light of definite wavelength.** *This is observed as a line in the spectrum of hydrogen atom.* Now, if the electron jumps down from the third to the first energy level having energies E_3 and E_1 respectively (Fig. 22), then the wavelength of the spectral line would be

$$\lambda' = \frac{hc}{E_3 - E_1}$$

Similarly, when the electron jumps from fourth (E_4) to first (E_1) or from fifth (E_5) to first (E_1) energy level, then the corresponding wavelengths of the emitted light will be :

$$\lambda'' = \frac{hc}{E_4 - E_1} \quad \text{and} \quad \lambda''' = \frac{hc}{E_5 - E_1}$$

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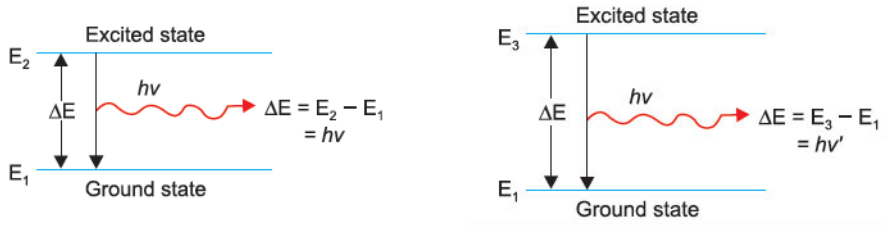

Fig. 22. Emission of radiation.

These will give different lines in the spectrum of the atom having definite wavelengths.

Thus, the different spectral lines in the spectra of atoms correspond to different transitions of electrons from higher energy levels to lower energy levels.

Simultaneous appearance of a large number of lines in the spectrum of hydrogen

This behaviour is quite curious and a question arises as to why hydrogen atom gives so many spectral lines although, it contains only one electron. In fact, any sample of hydrogen gas contains a large number of atoms and when energy is supplied by passing electric discharge, the electrons in different hydrogen atoms absorb different amounts of energies. Therefore, these are raised to different energy states. For example, the electrons in some atoms may jump to second energy level (L), while in others may be raised to third (M), fourth (N), fifth (O) energy levels and so on. Now, the excited electrons come back from the higher energy levels to the ground state in one or more jumps.

For example, let us consider some electrons present in fourth energy level (n = 4). Some of these electrons may directly jump to ground state (route a), others may first jump to second level and then to first (route b) while some others may first drop to third level and then finally to the first level either directly or first to second level (routes c and d). These four routes are shown in Fig. 23. When these excited electrons jump back to various lower energy levels, they emit different amounts of energies. This results into different lines depending upon the difference in energies of the levels concerned.

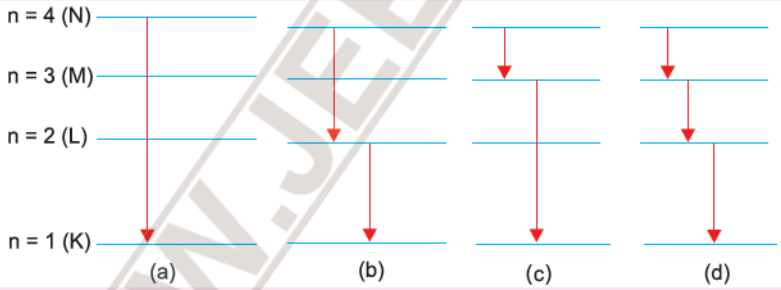

Fig. 23. Different routes to the ground state from n = 4.

For example, when the electron jumps from all the energy levels higher than n = 1, *i.e.*, n = 2, 3, 4, 5.... to n = 1 energy level, the lines obtained fall in the ultra-violet region. These lines are called **Lyman series.**

Similarly, the lines obtained when the electron jumps to second energy level (n = 2) from higher energy levels (n = 3, 4, 5, 6) fall in the visible region. These are called **Balmer series.**

In a similar manner, the transitions from higher energy levels to n = 3 produce **Paschen series.** Similarly, **Brackett** and **Pfund series** correspond to jumps from higher energy levels to n = 4 and n = 5 energy levels respectively.

The origin of series of transitions in the hydrogen spectrum are shown in Fig. 24.

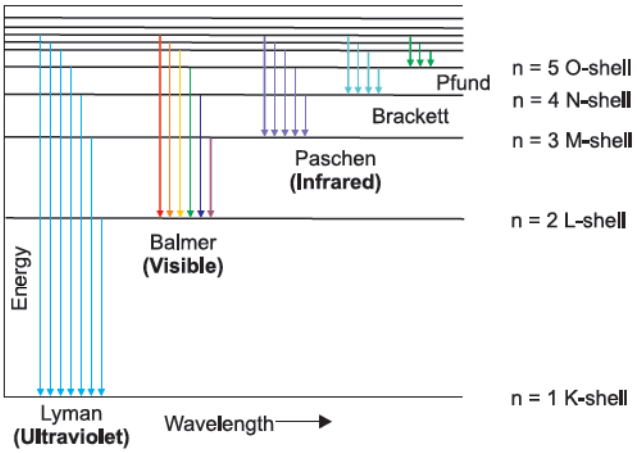

Fig. 24. Generation of spectral series in hydrogen spectrum.

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These are also summarized below:

Lyman series	From $n = 2, 3, 4, 5...$ to $n = 1$
Balmer series	From $n = 3, 4, 5, 6...$ to $n = 2$
Paschen series	From $n = 4, 5, 6, 7...$ to $n = 3$
Brackett series	From $n = 5, 6, 7,.....$to $n = 4$
Pfund series	From $n = 6, 7, 8, ...$to $n = 5$

KNOWLEDGE PLUS

The sixth series in the hydrogen spectrum was reported by Curtis J. Humphrey in 1953. It was named **Humphrey series** and are produced when the electron in the hydrogen atom jumps to 6th energy level ($n = 6$) from higher energy levels ($n = 7, 8, 9...$). For these lines,

$$\nu = R_H\left(\frac{1}{6^2}-\frac{1}{n_2^2}\right) \text{ where } n_2 = 7, 8, 9...$$

These lines lie in the far infra red region.

NOTE

In general, the number of emission lines when an electron jumps from n_2 level to n_1 level are given by the relation :

$$\frac{(n_2-n_1)(n_2-n_1+1)}{2}$$

For example, in the Lyman series when an electron drops from fifth level ($n_2 = 5$) to ground state ($n_1 = 1$), then

$$\text{No. of spectral lines} = \frac{(5-1)(5-1+1)}{2} = \frac{20}{2} = 10$$

These lines correspond to

$5 \longrightarrow 4, 5 \longrightarrow 3, 5 \longrightarrow 2, 5 \longrightarrow 1$ (4 lines)
$4 \longrightarrow 3, 4 \longrightarrow 2, 4 \longrightarrow 1$ (3 lines)
$3 \longrightarrow 2, 3 \longrightarrow 1$ (2 lines)
$2 \longrightarrow 1$ (1 lines)
Total (10 lines)

Similarly, total spectral lines in Balmer series ($n_1 = 2$) from 5th energy level ($n_2 = 5$) will be

$$\text{No. of spectral lines} = \frac{(5-2)(5-2+1)}{2} = 6$$

These lines correspond to

$5 \longrightarrow 4, 5 \longrightarrow 3, 5 \longrightarrow 2$ (3 lines)
$4 \longrightarrow 3, 4 \longrightarrow 2$ (2 lines)
$3 \longrightarrow 2$ (1 lines)
Total (6 lines)

3. Bohr's theory helped in calculating the energy of the electron in a particular orbit of hydrogen atom. On the basis of the postulates, Bohr derived a mathematical expression for the energy of an electron moving in a particular orbit of hydrogen atom. He pictured hydrogen atom as a system consisting of a single electron of mass m and negative charge e, revolving in a circular orbit. The energy of the electron in the nth orbit has been found to be

$$E_n = -R_H\left(\frac{1}{n^2}\right) \quad n = 1, 2, 3 .....$$

where R_H is called Rydberg constant and it is equal to $\frac{2\pi^2me^4}{h^2}$ so that

$$E_n = -\frac{2\pi^2me^4}{n^2h^2}$$

Substituting the values of m, e and h, the above expression becomes

$$E_n = -\frac{2.18\times10^{-18}}{n^2} \text{ J per atom}$$

$$\text{or} = -\frac{13.595\ eV}{n^2} \text{ per atom}$$

$(\because 1\ eV = 1.6022 \times 10^{-19}\ J)$

$$\text{or} = -\frac{1311.8}{n^2} \text{ kJ mol}^{-1} \quad \text{or} \approx -\frac{1312}{n^2} \text{ kJ mol}^{-1}$$

Thus, for each value of n, there exists a possible energy level for the electron. Substituting the values of n as 1, 2, 3, 4... in the above relation, we get the energy of electron in various energy levels of hydrogen atom. These integral numbers ($n = 1, 2, 3$ .....) expressing stationary states for electron are known as **principal quantum number.** The values for energies for first four orbits are given in Table 3.

Table 3. The energies of electron in different orbits of hydrogen atom

Orbit (n)	1	2	3	4
Energy (E) (kJ mol^{-1})	−1311.8	−327.9	−145.7	−82.0

NOTE

It is clear from the table that as the value of n increases, the energy difference between successive energy levels decreases. Hence

$E_2 - E_1 > E_3 - E_2 > E_4 - E_3$ and so on.

Energy expression for hydrogen like ions

The energy expression for hydrogen like ions may be written as :

$$E_n = -\frac{2\pi^2me^4Z^2}{n^2h^2}$$

$$\text{or} \quad = -2.18 \times 10^{-18}\left(\frac{Z^2}{n^2}\right) \text{ J per atom}$$

$$E_n = -1311.8\left(\frac{Z^2}{n^2}\right) \text{ kJ mol}^{-1}$$

where Z is the nuclear charge which is equal to atomic number. For example, for He^+, Z = 2; for Li^{2+}, Z = 3.

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Now, question arises as to why the energy of the electron in an atom is negative. This may be explained as follows :

Significance of negative electronic energy. It is clear from the above relation that the energy of an electron in the hydrogen atom is *negative*. What does this negative sign convey ? The negative sign of energy means that the energy of the electron in the atom is lower than the energy of a free electron at rest. A free electron at rest is an electron that is at sufficiently far away from the nucleus and its energy is **assumed** to be **zero**. Mathematically, it corresponds to setting n equal to infinity in the equation so that $E_\infty = 0$. As the electron moves closer to the nucleus due to electrostatic attraction, work is done by the electron itself and hence energy is released. Consequently, its energy decreases and it takes energy values less than zero, which means negative values. The negative sign also indicates that the electron is bound to the nucleus and a hydrogen atom is in a stable state in comparison to a state where electron is sufficiently far away from the nucleus.

Bohr radius

We can also calculate the radius of each circular orbit. According to Bohr's model, radius of nth orbit is

$$r_n = \frac{n^2h^2}{4\pi^2me^2Z}$$

$$\boldsymbol{r_n = a_0n^2} \qquad \text{[For hydrogen atom (Z = 1)]}$$

where $a_0 = 52.9$ pm.

Thus, the radius of first stationary state called the Bohr radius is 52.9 pm (or 0.0529 nm or 0.529 Å). Thus, for H atom,

radius of first orbit is **52.9 pm.**

Similarly, for second orbit,

$n = 2, \quad r_2 = 52.9 \times (2)^2$

$= 52.9 \times 4 = 211.6$ pm

For third orbit

$n = 3, \quad r_3 = 52.9 \times (3)^2 = 52.9 \times 9$

or $= 476.1$ pm

Normally, the electron in hydrogen atom is found in $n = 1$ orbit. As the value of n increases, the value of r will increase. This means that the electron will be present away from the nucleus.

Similarly, **for hydrogen like ions**, the radii may be given by the expression,

$$\boldsymbol{r_n = \frac{a_0n^2}{Z}}$$

$$\text{or} \quad r_n\,(\text{H-like}) = \frac{r_n\,(\text{H-atom})}{Z}$$

$$\text{or} \quad r_n = \frac{52.9\,n^2}{Z} \text{ pm}$$

$$\text{or} \quad r_n = \frac{0.0529\,n^2}{Z} \text{ nm}$$

where Z is the nuclear charge.

Velocity of electron in any orbit

The velocity of electron in any orbit is given by the expression

$$v = \frac{nh}{2\pi mr}$$

If we substitute the value of r, we get

$$v = \frac{2\pi e^2Z}{nh}$$

$$\text{or} \quad v = \frac{2.19 \times 10^6 Z}{n} \text{ m s}^{-1}$$

The velocities of the electrons in different orbits may be given as :

$$v_n = v_0 \times \frac{Z}{n}$$

where v_0 is the velocity of the electron in the first orbit of hydrogen atom and $v_0 = 2.19 \times 10^6$ ms^{-1}.

No. of revolutions made by an electron around nucleus

$$= \frac{\text{Velocity of electron}}{\text{Circumference of orbit}} = \frac{v}{2\pi r}$$

Substituting the value of r, we get

$$\text{No. of revolutions} = \frac{2\pi mv Ze^2}{n^2h^2}$$

Explanation of Line Spectrum of Hydrogen

Line spectrum observed in case of hydrogen atom can be quantitatively explained using Bohr's model. When an electron jumps from a lower orbit to a higher orbit, it absorbs energy. When the electron jumps from higher orbit to lower orbit, it emits energy.

The amount of energy absorbed or emitted when an electron jumps from orbit n_i (initial orbit) to orbit n_f (final orbit) may be given as

$$\Delta E = E_f - E_i$$

Now, $E_f = -\frac{R_H}{n_f^2}$ and $E_i = -\frac{R_H}{n_i^2}$

$$\therefore \Delta E = \left(-\frac{R_H}{n_f^2}\right) - \left(-\frac{R_H}{n_i^2}\right)$$

$$= R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= \mathbf{2.18 \times 10^{-18}\,J}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

The frequency (ν) associated with the absorption or emission of photon will be

$$\Delta E = h\nu \quad \text{or} \quad \nu = \frac{\Delta E}{h} \text{ so that}$$

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$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= \frac{2.18\times10^{-18}\,J}{6.626\times10^{-34}\,Js}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= \mathbf{3.29 \times 10^{15}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)\mathbf{Hz}$$

In terms of wave number, $\bar{\nu} = \frac{\nu}{c}$

$$\bar{\nu} = \frac{\nu}{c} = \frac{R_H}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= \frac{3.29\times10^{15}\,s^{-1}}{3\times10^{8}\,ms^{-1}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= \mathbf{1.09677 \times 10^{7}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)\mathbf{m^{-1}}$$

In case of absorption spectrum,

$$n_f > n_i$$

the term $\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$ becomes positive so that ΔE is positive and hence energy is absorbed.

In case of emission spectrum,

$$n_f < n_i$$

the term $\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$ becomes negative so that ΔE is negative and energy is released.

The above expression is similar to that used by Rydberg which he derived empirically using the experimental data available at that time. Further, it is clear that each spectral line whether in absorption or emission spectrum can be associated to a particular transition in hydrogen atom. In case of large number of hydrogen atoms present in a sample, different possible transitions can be observed (as already discussed) giving large number of spectral lines. The intensity or brightness of spectral lines depend upon the number of photons of same wavelength or frequency absorbed or emitted.

Ionization energy of hydrogen atom and hydrogen like ions

Ionization energy is the energy required to remove the electron completely from the atom so as to convert it to a positive ion. This means that it is the energy absorbed by the electron in the ground state ($n = 1$) so as to jump to infinity $n = \infty$. Thus, for H-atom, it can be calculated as

$$E_n = -\frac{2.18\times10^{-18}}{n^2}\,J\ atom^{-1}$$

or $$= -\frac{1311.8}{n^2}\,kJ\ mol^{-1}$$

$$I.E. = E_\infty - E_1$$

$$= 0 - (-2.18 \times 10^{-18})$$

$$= \mathbf{2.18 \times 10^{-18}\ J\ atom^{-1}}$$

or $$= 0 - (-1311.8)\ kJ\ mol^{-1}$$

$$= \mathbf{1311.8\ kJ\ mol^{-1}}$$

For H-like ions,

$$E_n = -\frac{2.18\times10^{-18}\,Z^2}{n^2}\,J\ atom^{-1}$$

or $$= -\frac{1311.8\,Z^2}{n^2}\,kJ\ mol^{-1}$$

$\therefore$ $I.E. = E_\infty - E_1$

$$= 0 - (-IE\,(H)\,Z^2)$$

$$= Z^2\,IE(H)$$

$\therefore$ For He^+, $Z = 2$

$$I.E. = 4 \times I.E.(H)$$

$$= 4 \times 1311.8$$

$$= \mathbf{5247.2\ kJ\ mol^{-1}}$$

For Li^{2+} $= Z = 3$

$$I.E. = 9 \times I.E.\ (H)$$

$$= 9 \times 1311.8$$

$$= \mathbf{11806.2\ kJ\ mol^{-1}}$$

It may be noted that ionization of He^+ is the second ionization energy of He and ionization energy of Li^{2+} is the third ionization energy of lithium atom.

SOLVED EXAMPLES

❑ **Example 20.**

What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ to $n = 2$ state in the hydrogen atom? ***N.C.E.R.T.***

Solution: The enery emitted during transition from $n = 5$ to $n = 2$ state,

$$\Delta E = 2.18 \times 10^{-18}\,J\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= 2.18 \times 10^{-18}\left(\frac{1}{5^2} - \frac{1}{2^2}\right)$$

$$= 2.18 \times 10^{-18}\left(\frac{4 - 25}{25 \times 4}\right)$$

$$= -4.578 \times 10^{-19}\,J$$

The negative sign indicates that the energy is emitted. For calculating wavelength and frequency, the minus sign may be omitted.

The frequency of emitted photon,

$$\nu = \frac{\Delta E}{h} = \frac{4.578\times10^{-19}\,J}{6.626\times10^{-34}\,Js}$$

$$= 6.91 \times 10^{14}\,s^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{3.0\times10^{8}\,ms^{-1}}{6.91\times10^{14}\,s^{-1}} = 4.34 \times 10^{-7}\,m \text{ or } \mathbf{434\ nm}$$

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❑ Example 21.

According to Bohr's theory, the electronic energy of hydrogen atom in the nth Bohr orbit is given by

$$E_n = -\frac{21.76 \times 10^{-19}}{n^2} \text{ J per atom}$$

Calculate the longest wavelength of light that will be needed to remove an electron from the third orbit of He^+ ion.

Solution: For hydrogen like ion, *i.e.*, He^+, the relation is :

$$E_n = -\frac{21.76 \times 10^{-19} Z^2}{n^2} \text{ J per atom}$$

where Z is atomic number. For He^+, Z = 2

Energy of He^+ ion in third orbit ($n = 3$)

$$E_3 = -\frac{21.76 \times 10^{-19} \times 4}{3^2} \text{ J}$$

Energy required to remove an electron from third Bohr orbit of He^+ ion is :

$$\Delta E = E_\infty - E_3$$

$$= 0 - \left(-\frac{21.76 \times 10^{-19} \times 4}{9}\right) \text{J}$$

$$= 9.67 \times 10^{-19} \text{ J}$$

Now, $\Delta E = \frac{hc}{\lambda}$

or $$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^8}{9.67 \times 10^{-19} \text{J}}$$

$$= 2.055 \times 10^{-7} \text{ m} = \mathbf{205.5 \text{ nm}}$$

❑ Example 22.

(i) The energy associated with the first orbit in the hydrogen atom is -2.17×10^{-18} J atom^{-1}. What is the energy associated with the fifth orbit ?

(ii) Calculate the radius of Bohr's fifth orbit for hydrogen atom. **N.C.E.R.T.**

Solution: (*i*) Energy associated with nth orbit in hydrogen atom is

$$E_n = -\frac{2.17 \times 10^{-18} \text{J}}{n^2} \text{ atom}^{-1}$$

∴ Energy associated with 5th orbit,

$$E_5 = -\frac{2.17 \times 10^{-18} \text{J}}{5^2}$$

$$= -8.68 \times 10^{-20} \text{ J}$$

(*ii*) Radius of Bohr's nth orbit is given as :

$$r_n = 0.0529\, n^2 \text{ nm}$$

∴ For $n = 5$

$r_5 = 0.0529 \times (5)^2$ nm = **1.3225 nm**

❑ Example 23.

Calculate the energy associated with the first orbit of He^+. What is the radius of this orbit ? **N.C.E.R.T.**

Solution: Energy of electron in nth orbit is

$$E_n = -\frac{2.18 \times 10^{-18} Z^2}{n^2} \text{J atom}^{-1}$$

For first orbit of He^+,

Z = 2, $n = 1$

$$E_1 = -\frac{2.18 \times 10^{-18}}{1^2} \times (2)^2 \text{ J atom}^{-1}$$

$$= \mathbf{-8.72 \times 10^{-18} J}$$

Radius of nth orbit is

$$r_n = \frac{0.0529\, n^2}{Z} \text{ nm}$$

$$\therefore \quad r_1 = \frac{0.0529 \times 1^2}{2} = \mathbf{0.02645 \text{ nm}}$$

❑ Example 24.

Radius of the fourth orbit in hydrogen atom is 0.85 nm. Calculate the velocity of the electron in this orbit (mass of electron = 9.1×10^{-31} kg).

Solution: From Bohr's postulate, the angular momentum (mvr) is given as :

$$mvr = \frac{nh}{2\pi} \text{ or } v = \frac{nh}{2\pi mr}$$

$n = 4$, $m = 9.1 \times 10^{-31}$ kg, $r = 0.85 \times 10^{-9}$ m

$$\therefore \quad v = \frac{4 \times 6.626 \times 10^{-34}}{2 \times \frac{22}{7} \times 9.1 \times 10^{-31} \times 0.85 \times 10^{-9}}$$

$$= \mathbf{5.45 \times 10^5 \text{ m s}^{-1}}$$

❑ Example 25.

The radius of first Bohr orbit of hydrogen atom is 0.529 Å. Calculate the radii of (i) the third orbit of He^+ ion and (ii) the second orbit of Li^{2+} ion.

Solution: Radius of *nth* Bohr orbit $r_n = \frac{n^2 h^2}{4\pi^2 m\, Ze^2}$

For hydrogen atom, Z = 1, first orbit $n = 1$

$$r_1 = \frac{h^2}{4\pi^2 me^2} = 0.529 \text{ Å}$$

(*i*) For He^+ ion, Z = 2, third orbit, $n = 3$

$$r_3(He^+) = \frac{3^2 h^2}{4\pi^2 m \times 2 \times e^2} = \frac{9}{2}\left[\frac{h^2}{4\pi^2 me^2}\right]$$

$$= \frac{9}{2} \times 0.529 = \mathbf{2.384 \text{ Å}}$$

(*ii*) For Li^{2+} ion, Z = 3, second orbit, $n = 2$

$$r_2(Li^{2+}) = \frac{2^2 h^2}{4\pi^2 m \times 3 \times e^2} = \frac{4}{3}\left[\frac{h^2}{4\pi^2 me^2}\right]$$

$$= \frac{4}{3} \times 0.529 = \mathbf{0.7053 \text{ Å}}$$

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Example 26.

Calculate the ratio of the radius of 2nd orbit of H atom and that of 3rd orbit.

Solution: The radius of nth orbit (r_n) of hydrogen atom is given as :

$$r_n = \frac{n^2h^2}{4\pi^2me^2}$$

$$r_n \propto n^2$$

Radius of second orbit $r_2 \propto 2^2$ or 4

Radius of third orbit, $r_3 \propto 3^2$ or 9

$$\therefore \quad \frac{r_2}{r_3} = \frac{4}{9}$$

Example 27.

The electronic energy of H atom is

$$E_n = -\frac{1.312\times10^6}{n^2}\text{J mol}^{-1}$$

Calculate

(i) First excitation energy of the electron in the hydrogen atom.

(ii) Ionization energy of the hydrogen atom.

Solution: (*i*) First excitation energy is the amount of energy required to excite the electron from ground state ($n = 1$) to $n = 2$ (first excited state).

$$\Delta E = E_2 - E_1$$

$$= -\frac{1.312\times10^6}{2^2} - \left(-\frac{1.312\times10^6}{1^2}\right)$$

$$= -3.28 \times 10^5 + 13.12 \times 10^5$$

$$= \mathbf{9.84 \times 10^5\ J\ mol^{-1}}$$

(*ii*) Ionization energy is the amount of energy required to remove the electron from $n = 1$ to $n = \infty$ *i.e.*

$$\Delta E = E_\infty - E_1$$

$$= 0 - (-1.312 \times 10^6)$$

$$= \mathbf{1.312 \times 10^6\ J\ mol^{-1}}$$

Example 28.

The ionization energy of He^+ is 8.72×10^{-18} J atom^{-1}. Calculate the energy of first stationary state of Li^{2+}.

Solution: Energy of electron in an orbit is

$$E_n = -\frac{2\pi^2me^4}{n^2h^2}(Z)^2 = -k\frac{Z^2}{n^2}$$

where k (constant) $= \dfrac{2\pi^2me^4}{h^2}$

$$\text{I.E. of } He^+ = E_\infty - E_1 = 0 - \left(-\frac{k(2)^2}{1^2}\right) = 4k$$

$$\therefore \quad 4k = 8.72 \times 10^{-18}\text{ J atom}^{-1}$$

$$\text{or} \quad k = \frac{8.72\times10^{-18}}{4} = 2.18\text{ J atom}^{-1}$$

For Li^{2+}, Z = 3 and first stationary state, $n = 1$.

$$\therefore \quad E_1 = -k\frac{Z^2}{n^2} = -\frac{2.18\times10^{-18}\times3^2}{1^2}$$

$$= \mathbf{-19.62 \times 10^{-18}\ J\ atom^{-1}.}$$

Practice Problems

25. What is the maximum number of emission lines when the excited electron of a H atom in n = 6 drops to the ground state ? **N.C.E.R.T.**

26. The energy difference between two electronic states is 399.1 kJ mol^{-1}. Calculate the wavelength and frequency of light emitted when an electron drops from a higher to a lower state. (Planck's constant, $h = 3.98 \times 10^{-13}$ kJ s mol^{-1}).

27. How much energy is required to ionise a H-atom if the electron occupies $n = 5$ orbit ? Compare your answer with the ionization energy of H atom. **N.C.E.R.T.**

28. Light of wavelength 1281.8 nm is emitted when an electron of H-atom drops from 5th to 3rd energy level. Calculate the wavelength of the photon emitted when electron falls from third to ground level.

29. What transition in the hydrogen spectrum would have the same wavelength on the Balmer transition, $n = 4$ to $n = 2$ of He^+ spectrum ?

30. Ionisation energy of hydrogen atom is 13.6 eV. What will be the ionisation energy of He^+ and Li^{2+} ions ?

31. What is the energy in joules required to shift the electron of the hydrogen from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of the light emitted when the electron returns to the ground state ? The ground state electron energy is -2.18×10^{-11} ergs.

32. Calculate the wave number for the longest wavelength transition in the Balmer series of atomic hydrogen. **N.C.E.R.T.**

33. The electronic energy in hydrogen atom is given as

$$E_n = -\frac{2.18\times10^{-18}\text{ J}}{n^2}$$

Calculate the energy required to remove an electron completely from $n = 2$ orbit. What is the longest wavelength of light in cm that can be used to cause this transition ? **N.C.E.R.T.**

Answers to Practice Problems

25. 15 lines
26. 300 nm, 1×10^{15} s^{-1}
27. 8.72×10^{-20} J, 2.18×10^{-18} J
28. 102.5 nm
29. $n = 2$ to $n = 1$
30. 54.4 eV, 122.4 eV
31. 2.09×10^{-18} J, 951 Å
32. 1.523×10^6 m^{-1}.
33. 3647 Å

Hints & Solutions on page 68

Bohr's Theory and Concept of Quantisation

A noticeable achievement of Bohr's theory of the structure of an atom was that it could predict the values of energies which an electron can have while revolving around the nucleus of hydrogen atom. According to Bohr, the electron in hydrogen atom can have energy values given by the relationship :

Energy of the electron $= -\dfrac{1311.8}{n^2}$ kJ mol^{-1},

where $n = 1, 2, 3, 4$ ...

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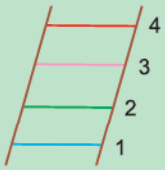
In other words, n cannot have fractional values so that the electron cannot have all possible values of energy but only those values for which n is a whole number. Thus, electron can take only certain fixed values of energy. It means that when an electron gains or loses energy, it does so in such a way that n has a value which is a whole number. In other words, electron does not gain or lose energy in a continuous manner but in jumps (or bursts). This led to the concept of **quantisation of energy** which means that *radiant energy is emitted or absorbed in bursts (or jumps) rather than as continuous flow*. From the above facts, it can be concluded that the energy of the electron is quantised.

KEY NOTE

The **quantisation** concept may seem to be mysterious but it is very easy to understand. The discrete energy levels in Bohr model may be compared with steps of a ladder. Imagine a ladder having steps labelled as 1, 2, 3, 4... from the bottom.

Your position on the ladder can only be on a step and never in between. These steps in a ladder are similar to energy levels (orbits) in an atom.



Definite steps (levels) in a ladder

Limitations of Bohr's Atomic Theory

Bohr's theory of atomic structure was quite successful in explaining the stability of atom and the line spectrum of hydrogen atom. However, several discrepancies were observed in this model. Some of the limitations of Bohr's model are :

1. *Bohr's model of an atom could not account for the finer details (doublet, two closely spaced lines) of the hydrogen spectrum observed using sophisticated spectroscopic techniques.*

2. *Bohr's model of an atom could not explain the line spectra of atoms containing more than one electron called multielectron atoms.* According to Bohr's theory, one and only one spectral line can originate from an electron between any two given energy levels. But, if a powerful spectroscope is used, certain single lines are found to split into a number of very closely related lines. The existence of such lines could not be explained on the basis of Bohr's theory.

3. *Bohr's theory failed to account for the effect of magnetic field on the spectra of atoms or ions.* It was observed that when the atom emitting radiations is placed in a strong magnetic field, each spectral line is further split into a number of lines. This phenomenon is known as **Zeeman effect.**

4. *Bohr's theory also could not explain the effect of electric field (known as **Stark effect**) on the spectra of atoms.*

5. *Bohr's theory does not provide any clue to explain the shapes of molecules arising out of the directional bonding between atoms.*

6. The main objection to the Bohr's theory came from the new principles namely *dual nature of matter* and *uncertainty principle*. They introduced the idea of wave character of electron in addition to its particle character and pointed out that the path of the motion of the electron cannot be well-defined. Thus, these overruled the Bohr's idea of well defined circular paths.

Thus, we find that Bohr's model was only partially successful. It explained some experimental results but was unable to account for many other features of the atom. Therefore, it was abandoned in the light of modern ideas regarding the wave characteristics of matter.

add on Conceptual Questions 1

CONCEPTUAL QA

Q. 1. What is the difference between a proton and a photon?

Ans. A proton is a positively charged nuclear particle having mass equal to that of an atom of hydrogen and one unit positive charge. Photon is the smallest particle of light having energy equal to $h\nu$.

Q. 2. How are frequency and wave number related to each other ?

Ans. Frequency $\nu = \frac{c}{\lambda}$ ..(*i*)

and wave number, $\bar{\nu} = \frac{1}{\lambda}$ ...(*ii*)

From (*i*) and (*ii*) $\nu = c\bar{\nu}$

Q. 3. Why are Bohr's orbits called stationary states ?

Ans. Stationary orbits means that the energies of the orbits in which the electrons revolve are fixed.

Q. 4. Which series of hydrogen spectrum lies in the visible region ?

Ans. Balmer series.

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Q. 5. To which Bohr's orbit in hydrogen atom, the electric transition corresponds to third line in the Balmer series ?

Ans. Fifth to second.

Q. 6. If the energy of an electron in the second Bohr orbit of H-atom is –E, what is the energy of the electron in the Bohr's first orbit ?

Ans. $E_n \propto \frac{1}{n^2}$ $\therefore E_1 \propto \frac{1}{1}$ and $E_2 \propto \frac{1}{4}$ $\therefore \frac{E_1}{E_2} = \frac{4}{1}$ or $E_1 = 4E_2$

If $E_2 = -E$, then $E_1 = -4E$.

Q. 7. What do you mean by saying that energy of the electron is quantized ?

Ans. This means that the electrons in an atom have only definite values of energies.

Q. 8. The magnitude of charge on the electron is 4.8×10^{-10} e.s.u. What is the charge on the nucleus of a helium atom ?

Ans. Helium nucleus contains 2 protons and charge of a proton is same as that of an electron. Therefore, the charge on the nucleus of a helium atom is $+ 2 \times 4.8 \times 10^{-10} = + 9.6 \times 10^{-10}$ e.s.u.

Q. 9. Which of the following relate to light as wave motion or stream of particles or both ?
(*i*) interference (*ii*) photoelectric effect (*iii*) $E = mc^2$ (*iv*) $E = h\nu$

Ans. (*i*) Wave motion (*ii*) Particles (*iii*) Particles (*iv*) both

Q. 10. Which transitions between Bohr orbits correspond to
(*i*) second line in the Balmer series and
(*ii*) first line in Brakett series of the hydrogen spectrum?

Ans. (*i*) From 4th orbit to 2nd orbit (*ii*) From 5th orbit to 4th orbit.

CONCEPTUAL QA

Q. 11. Arrange the following types of radiations in increasing order of frequency ?
(*a*) radiation from microwave oven
(*b*) amber light from traffic signal
(*c*) radiation from FM radio
(*d*) cosmic rays from outer space
(*e*) X-rays ***N.C.E.R.T.***

Ans. Cosmic rays < X-rays < amber light < microwave < FM

Q. 12. Wavelengths of different radiations are given below :

$\lambda(A) = 300$ nm, $\lambda(B) = 300$ μm, $\lambda(C) = 3$ nm, $\lambda(D) = 30$ Å

Arrange these radiations in the increasing order of their energies.

Ans. The wavelengths in m are :

$\lambda(A) = 300 \text{ nm} = 300 \times 10^{-9}$ m, $\lambda(B) = 300$ μm $= 300 \times 10^{-6}$ m

$\lambda(C) = 3 \text{ nm} = 3 \times 10^{-9}$ m, $\lambda(D) = 30$ Å $= 30 \times 10^{-10}$ m or 3×10^{-9} m

Since $E \propto \frac{1}{\lambda}$, the increasing order of energies is B < A < C = D.

Q. 13. What is the main difference between electromagnetic wave theory and Planck's quantum theory?

Ans. According to electromagnetic wave theory, energy is emitted or absorbed continuously whereas according to Planck's quantum theory, energy is emitted or absorbed discontinuously i.e., in certain definite packets of energy called **quanta**.

Q. 14. Energy of an electron in H atom in ground state is 13.6 eV. What is the value in first excited state?

Ans. Energy of an electron in n^{th} level of H–atom is

$$E_n = -\frac{13.6}{n^2} eV$$

The energy in first excited state ($n = 2$), $E_2 = -\frac{13.6}{2^2} eV = -3.4$ eV.

Q. 15. Although α-particle have a larger charge, but β-particles are deflected more than α-particles in a given electric field. Why ?

Ans. β-particles have very-very small mass and therefore, their charge to mass ratio is large despite their lower charge. Thus, these are deflected more.

Q. 16. What are nucleons ?

Ans. The protons and neutrons present in the nucleus are collectively called nucleons.

Q. 17. Which of the following has lowest frequency ?
X-rays, γ-rays, microwaves

Ans. Microwaves

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Advanced Level PROBLEMS Accelerate Your Potential (for JEE Advance)

Problem 1. A certain metal was irradiated with light of frequency 3.2×10^{16} sec^{-1}. The photoelectrons emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with a light of frequency 2×10^{16} sec^{-1}. Calculate the threshold frequency of the metal.

Solution Kinetic energy of emitted photoelectrons is

$$\text{K.E.} = h\nu - h\nu_o = h(\nu - \nu_o)$$

For the light of frequency 3.2×10^{16} sec^{-1}

$$\text{K.E}_1 = h(3.2 \times 10^{16} - \nu_o)$$

For the light of frequency 2×10^{16} sec^{-1}

$$\text{KE}_2 = h(2.0 \times 10^{16} - \nu_o)$$

It is given that $\text{KE}_1 = 2\ \text{KE}_2$

$$\therefore \quad h(3.2 \times 10^{16} - \nu_o) = 2h(2.0 \times 10^{16} - \nu_o)$$

$$3.2 \times 10^{16} - \nu_o = 2(2.0 \times 10^{16} - \nu_o)$$

$$3.2 \times 10^{16} - \nu_o = 4.0 \times 10^{16} - 2\nu_o$$

$$-\nu_o + 2\nu_o = (4.0 - 3.2) \times 10^{16}$$

or $$\nu_o = 0.8 \times 10^{16}$$

or $$= \mathbf{8.0 \times 10^{15}\ sec^{-1}}$$

Problem 2. Calculate the wavelength of the spectral line obtained in the spectrum of Li^{2+} ion when transition takes place between two levels whose difference is 2 and the sum is 4.

Solution Suppose the transition takes place between two levels n_1 and n_2 and

$$n_2 - n_1 = 2 \quad ...(i)$$

and $$n_2 + n_1 = 4 \quad ...(ii)$$

In order to solve for the values of n_1 and n_2, add eqn (i) and (ii)

$$2n_2 = 6 \quad \text{or} \quad n_2 = 3$$

and $$3 - n_1 = 2 \quad \text{or} \quad n_1 = 1$$

According to Rydberg equation

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)Z^2$$

For Li^{2+}, $Z = 3$, $R = 109677$ cm^{-1}

$$\frac{1}{\lambda} = 109677\left(\frac{1}{1^2} - \frac{1}{3^2}\right) \times 3^2$$

$$= 109677\left(\frac{1}{1} - \frac{1}{9}\right) \times 9$$

$$= 109677 \times \frac{8}{9} \times 9$$

$$\frac{1}{\lambda} = 109677 \times 8\ \text{cm}^{-1} = 877416\ \text{cm}^{-1}$$

or $$\lambda = \frac{1}{877416\ \text{cm}^{-1}} = 1.14 \times 10^{-6}\ \text{cm}$$

or $$\lambda = 1.14 \times 10^{-8}\ \text{m} \quad \text{or} \quad \mathbf{11.4\ nm}$$

Problem 3. The angular momentum of an electron in a Bohr's orbit of hydrogen atom is 4.218×10^{-34} kg m^{2}s^{-1}. Calculate the wavelength of the spectral line emitted when electron falls from this level to next lower level.

Solution Angular momentum of an electron in a Bohr's orbit of H-atom.

$$mvr = \frac{nh}{2\pi}$$

$$4.218 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1} = \frac{n \times 6.626 \times 10^{-34}\ \text{kg m}^2\text{s}^{-2}}{2 \times \frac{22}{7}}$$

or $$n = \frac{4.218 \times 10^{-34} \times 2 \times 22}{6.626 \times 10^{-34} \times 7} = 4$$

Now $$\bar{\nu} = \frac{1}{\lambda} = 109678\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\ \text{cm}^{-1}$$

The spectral line when electron falls from 4th level to 3rd level so that

$$n_2 = 4, n_1 = 3$$

$$\frac{1}{\lambda} = 109678\left(\frac{1}{3^2} - \frac{1}{4^2}\right)\ \text{cm}^{-1}$$

$$\frac{1}{\lambda} = 109678\left(\frac{16 - 9}{9 \times 16}\right)\ \text{cm}^{-1}$$

$$\frac{1}{\lambda} = 109678 \times \frac{7}{9 \times 16}\ \text{cm}^{-1}$$

$$\therefore \quad \lambda = \frac{9 \times 16}{109678 \times 7} = \mathbf{1.876 \times 10^{-4}\ cm}$$

Problem 4. Calculate the ratio of wavelength of first spectral line of Lyman and Balmer series of hydrogen spectrum.

Solution According to Rydberg equation,

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For first line of Lyman series

$$n_1 = 1, n_2 = 2$$

$$\frac{1}{\lambda_L} = R\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

$$\frac{1}{\lambda_L} = R \times \frac{3}{4} \text{ or } \lambda_L = \frac{4}{3R}$$

For first line of Balmer series

$$n_1 = 2, n_2 = 3$$

$$\frac{1}{\lambda_B} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5R}{36}$$

$$\therefore \lambda_B = \frac{36}{5R}$$

Now $$\frac{\lambda_L}{\lambda_B} = \frac{4}{3R} \times \frac{5R}{36} = \frac{5}{27}$$

Ratio of Lyman and Balmer series = **5 : 27.**

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Problem 5. **Calculate the frequency, energy and wavelength of radiation corresponding to the spectral line of lowest frequency in Lyman series in the spectra of hydrogen atom. Also calculate the energy for the corresponding line in the spectra of Li^{2+}. ($R = 1.09678 \times 10^7\ m^{-1}$, $c = 3 \times 10^8\ m\ s^{-1}$, $h = 6.625 \times 10^{-34}\ J\ s$).**

Solution According to Rydberg equation,

$$\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For lowest frequency (or energy) in Lyman series :

$$n_1 = 1, n_2 = 2$$

$$\therefore \quad \bar{\nu} = 1.09678 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

$$= 1.09678 \times 10^7 \times \frac{3}{4}$$

$$= 0.8226 \times 10^7\ m^{-1}$$

Now, $\quad \bar{\nu} = \dfrac{1}{\lambda}$

$$\therefore \quad \lambda = \frac{1}{\bar{\nu}} = \frac{1}{0.8226 \times 10^7}$$

$$= \mathbf{1.216 \times 10^{-7}\ m}$$
$$= \mathbf{121.6\ nm}$$

Now, $\quad \nu = \dfrac{c}{\lambda}$

$$= \frac{3.0 \times 10^8}{1.216 \times 10^{-7}}$$

$$= 2.47 \times 10^{15}\ s^{-1}$$

Now $\quad E = h\nu$
$$= 6.625 \times 10^{-34} \times 2.47 \times 10^{15}$$
$$= \mathbf{1.636 \times 10^{-18}\ J}$$

For $\quad Li^{2+}, Z = 3$

$$\therefore \quad E_{Li^{2+}} = (3)^2 \times 1.636 \times 10^{-18}$$
$$= \mathbf{1.47 \times 10^{-17}\ J}.$$

Problem 6. **Calculate the value of Rydberg constant, R if for He^+ ions the difference between the longest wavelength line of Balmer series and Lyman series is 133.8 nm.**

Solution For He^+ ion spectrum

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where R is Rydberg constant and Z = 2 (for He^+ ion)

For longest wavelength line in Balmer series,

$$n_1 = 2, \quad n_2 = 3$$

$$\frac{1}{\lambda_B} = R(2)^2\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$= 4R\left(\frac{1}{4} - \frac{1}{9}\right) = \frac{4R \times 5}{36}$$

or $\quad \lambda_B = \dfrac{9}{5R}$

For longest wavelength line in Lyman series,

$$n_1 = 1, \quad n_2 = 2,$$

$$\frac{1}{\lambda_L} = R(2)^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

$$= 4R\left(\frac{1}{1} - \frac{1}{4}\right) = \frac{4R \times 3}{4}$$

or $\quad \lambda_L = \dfrac{1}{3R}$

Now $\quad \lambda_B - \lambda_L = 133.8 \times 10^{-9}\ m$

$$133.8 \times 10^{-9} = \frac{9}{5R} - \frac{1}{3R}$$

$$= \frac{1}{R}\left(\frac{9}{5} - \frac{1}{3}\right) = \frac{1}{R}\left(\frac{27-5}{15}\right)$$

or $\quad 133.8 \times 10^{-9} = \dfrac{1}{R} \times \dfrac{22}{15}$

$$\therefore \quad R = \frac{22}{15 \times 133.8 \times 10^{-9}} = \mathbf{1.0961 \times 10^7\ m^{-1}}$$

Problem 7. **Which energy level in Li^{2+} has same energy as the fourth energy level of hydrogen atom?**

Solution Let nth level of Li^{2+} has the same energy as the fourth energy level of H atom.

Energy of nth level of Li^{2+}

$$E_{Li^{2+}}(n) = \frac{E_{Li^{2+}}(1)}{n^2} \qquad (i)$$

Energy of fourth level of H-atom

$$E_H(4) = \frac{E_H(1)}{4^2} \qquad (ii)$$

$$E_{Li^{2+}}(1) = E_H(1) \times 3^2\ (\because Z = 3) \qquad (iii)$$

Now $\quad \dfrac{E_H(1)}{4^2} = \dfrac{E_{Li^{2+}}(1)}{n^2}$

$$\frac{E_H(1)}{4^2} = \frac{E_H(1) \times 3^2}{n^2}$$

or $\quad n^2 = 3^2 \times 4^2$

$$\therefore \quad n = \mathbf{12}$$

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Problem 8. Energy of an electron in hydrogen atom is given as:

$$E_n = -\frac{2\pi^2 me^4}{n^2h^2} = -\frac{1.312 \times 10^6}{n^2} \text{ J mol}^{-1}$$

(*i*) Calculate the ionisation energy of H-atom.

(*ii*) Compare the shortest wavelength emitted by hydrogen atom and He^+ ion.

Solution

(*i*) Ionisation energy of H-atom corresponds to energy change when electron is removed from $n_1 = 1$ to $n_2 = \infty$

$$E_1 = -\frac{1.312\times10^6}{1} \text{ J mol}^{-1}, E_\infty = 0$$

$\therefore$ ΔE = Ionisation energy of H-atom

$= E_\infty - E_1$

$= 0 - (-1.312 \times 10^6) = \mathbf{1.312 \times 10^6\ J}$

(*ii*) The shortest wavelength corresponds to electron jump from $n_2 = \infty$ to $n_1 = 1$ for H-atom and He^+ ion.

$$E_H = 0 - \left(-\frac{2\pi^2 me^4}{1^2h^2}\right) = \frac{2\pi^2 me^4}{h^2}$$

$$E_{He^+} = 0 - \left(-\frac{2\pi^2 me^4 (2)^2}{1^2h^2}\right) = \frac{8\pi^2 me^4}{h^2}$$

($Z = 2$ for He^+ ion)

$$\frac{E_{He^+}}{E_H} = \frac{8\pi^2 me^4}{h^2} \times \frac{h^2}{2\pi^2 me^4} = 4$$

Now, $E = h\nu = \frac{hc}{\lambda}$ or $\lambda = \frac{hc}{E}$

$$\lambda_H = \frac{hc}{E_H}$$

$$\lambda_{He^+} = \frac{hc}{E_{He^+}}$$

$$\frac{\lambda_H}{\lambda_{He^+}} = \frac{E_{He^+}}{E_H} = 4 \text{ or } \lambda_H = 4\lambda_{He^+}$$

Wavelength emitted by H-atom is **four times** that of He^+ ion.

MODERN CONCEPT OF STRUCTURE OF ATOM : QUANTUM MECHANICAL MODEL

To overcome the shortcomings of the Bohr's model, attempts were made to develop a more suitable and general model for an atom. Two important developments which contributed significantly in the formulation of a new model were:

1. Dual nature of matter
2. Heisenberg uncertainty principle.

1. Dual Nature of Matter

Einstein has suggested that light can behave as a wave as well as like a particle *i.e.*, it has dual character. In 1924, de-Broglie suggested that just as light exhibits wave and particle properties, all microscopic material particles such as electrons, protons, atoms, molecules, etc. have also dual character. They behave as a particle as well as a wave. This means that an electron which has been regarded as a particle also behaves like a wave. Thus, according to **de Broglie,**

all material particles in motion possess wave characteristics.

According to de-Broglie, the wavelength associated with a particle of mass m, moving with velocity v is given by the relation,

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

where h is Planck's constant, v is the velocity and p ($= mv$) is momentum of the particles. The waves associated with material particles are called **matter waves** or **de Broglie waves.**

Derivation of de Broglie Relationship

The relationship may be derived by combining the mass-energy relationships proposed by *Max Planck* and *Einstein.*

According to Planck, photon of light having energy E is associated with a wave of frequency ν as :

$$E = h\nu \quad ...(i)$$

According to Einstein, mass and energy are related as :

$$E = mc^2 \quad ...(ii)$$

where c is the velocity of light.

Combining the above two relations in eqs. (*i*) and (*ii*), we get :

$$h\nu = mc^2$$

Now, since $\nu\lambda = c$

or $\nu = \frac{c}{\lambda}$

$\therefore$ $\frac{hc}{\lambda} = mc^2$

Cancelling c, $\frac{h}{\lambda} = mc$

or $\lambda = \frac{h}{mc}$

The equation is valid for a photon. de-Broglie suggested that on substituting the mass of the particle m and its velocity v in place of velocity of light c, the equation can also be applied to material particles.

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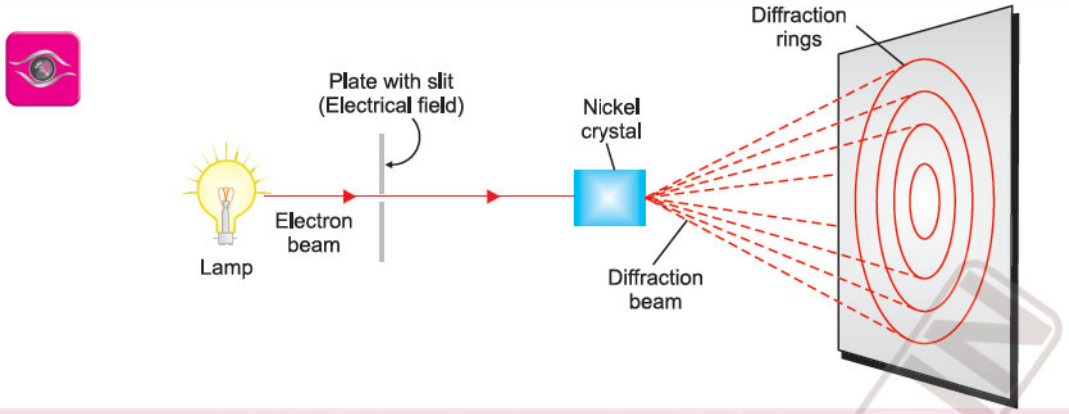

Fig. 25. Electron diffraction experiment by Davisson and Germer.

Thus, the wavelength of material particles, λ is :

$$\lambda = \frac{h}{mv}$$

This equation is known as **de-Broglie's equation.**

or $$\lambda = \frac{h}{p}$$

$$= \frac{\text{Planck's constant}}{\text{Momentum}}$$

where p stands for the momentum (mv) of the particle. Since h is constant,

$$\therefore \quad \lambda \propto \frac{1}{\text{Momentum}}$$

It means that the wavelength of a particle in motion is inversely proportional to its momentum.

The equation is known as **de-Broglie relation.**

Justification for the dual nature of electrons

The particle and wave nature of electrons can be justified on the basis of following observations :

1. Particle nature. Electrons exhibit the characteristics of particles. They have definite mass, energy, momentum and charge. When an electron strikes a zinc sulphide screen, it produces a spot of light known as **scintillation.** It has been observed that each striking electron produces only one scintillation point. This indicates that the scintillation and, therefore, the striking electron must be localised and not spread out like a wave. This suggests that the electron behaves as a particle.

2. Wave nature. The wave nature of electrons was experimentally verified by Davisson and Germer in 1927 and George Thomson in 1928.

Experimental Verification of Wave Character of Electrons

(*i*) Davisson and Germer's experiment. Davisson and Germer subjected the streams of electrons emitted from a tungsten filament to the influence of strong electrical field so as to accelerate the speed of the electrons. When these electrons were made to strike against nickel crystals, concentric dark and bright rings were formed on screen (Fig. 25).

These rings were called the *diffraction rings* and this phenomenon was known as **diffraction.** This diffraction pattern of electrons by crystals was similar to that observed for X-rays. The diffraction patterns of X-rays and that of electrons are shown in Fig. 26 (*a*) and (*b*) respectively. The similarity of these two patterns indicates that the electrons behave like X-rays.

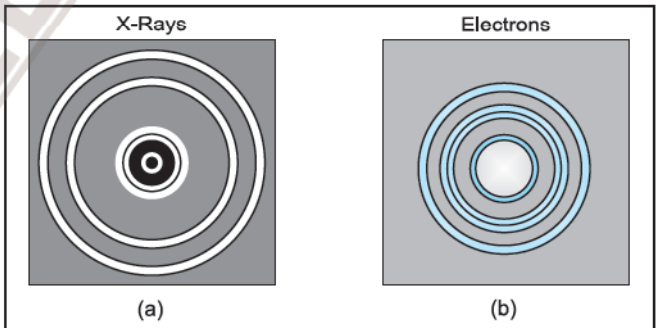

Fig. 26. Diffraction pattern obtained from (*a*) X-ray and (*b*) electrons.

Since X-rays have wave character, therefore, *the electrons must also have wave character associated with them.* Moreover, the wavelengths of the electrons as determined by the diffraction experiments were found to be in agreement with the values calculated from de-Broglie's equation.

(*ii*) Thomson's experiment. G.P. Thomson, in 1928 performed similar experiments with thin gold foil in place of nickel crystal and observed diffraction pattern as before. This confirmed the wave nature of the electron. The diffraction patterns were also observed with protons, neutrons, hydrogen atoms, etc. This confirms that all material particles have wave character and hence dual character.

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KEY NOTE

- The particle character of matter (*e.g.* electron) had been established from a number of experiments and its wave character was confirmed by diffraction and interference experiments.
- The wave like character of electron helped in making **electron-microscope** which is very powerful tool in modern scientific research because it achieves magnification of 15 million times. The electron microscope utilises the wave like behaviour of electrons just as an ordinary microscope utilises the wave like nature of light.
- Protons, neutrons, hydrogen atoms or even fullerene molecules (C_{60}) have also been shown to have wave character.

Significance of de-Broglie Relationship

Although the dual nature of matter is applicable to all material objects but it is significant for microscopic bodies only. For large bodies, the wavelengths of the associated waves are very small and cannot be measured by any of the available methods. Therefore, practically these bodies are said to have no wavelengths. Thus, any material body in motion can have wavelength but it is measurable or significant only for microscopic bodies such as electron, proton, atom or molecule. This may be illustrated as follows :

The wavelength of an electron with mass 9.11×10^{-31} kg and moving with the velocity of 10^6 m s^{-1} is 7.28×10^{-10} m as shown below:

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{(9.11 \times 10^{-31}\ \text{kg}) \times (10^6\ \text{m s}^{-1})}$$

$$= 7.28 \times 10^{-10}\ \text{m} \qquad [\text{J} = \text{kg m}^2\ \text{s}^{-2}]$$

This wavelength associated with the moving electron is of the same order of magnitude as of X-rays which can be easily measured.

On the other hand, the wavelength associated with a ball, for example, weighing 10 g and moving with the same velocity as that of electron (10^6 m s^{-1}) is only 6.63×10^{-38} m as shown below :

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{(10 \times 10^{-3}\ \text{kg}) \times (10^6\ \text{m s}^{-1})} = 6.63 \times 10^{-38}\ \text{m}$$

This wavelength is shorter than any electro-magnetic radiation and cannot be measured by any known method. Therefore, it is difficult to grasp the idea of waves associated with the moving ball. In other words, we can say that the ball does not have waves associated with it. Similarly, the other large bodies are said to be associated with waves but their wavelengths are too small to be measured by any conceivable method.

Estimating the de-Broglie wavelength

Let an electron of charge e be accelerated by a potential V. Then the kinetic energy acquired by the electron which is accelerated from rest by passing through a potential difference V is eV. The kinetic energy of the electron moving with velocity v is also written as $\frac{1}{2}mv^2$. Thus,

$$\frac{1}{2}mv^2 = Ve \quad \text{or} \quad v = \left(\frac{2Ve}{m}\right)^{\frac{1}{2}}$$

Substituting the value of v in the de-Broglie equation, we get

$$\lambda = \frac{h}{m(2Ve/m)^{\frac{1}{2}}} \text{ or } \frac{h}{(2Vem)^{\frac{1}{2}}}$$

Substituting the numerical values of various quantities :

$h = 6.626 \times 10^{-34}$ kg m^2 s^{-1}, $e = 1.602 \times 10^{-19}$ C, $m = 9.11 \times 10^{-31}$ kg

$$\lambda = \frac{6.626 \times 10^{-34}\text{kg m}^2\text{s}^{-1}}{\left[2 \times \text{V} \times \left(1.602 \times 10^{-19}\text{C}\right) \times \left(9.11 \times 10^{-31}\text{kg}\right)\right]^{\frac{1}{2}}}$$

$$= \frac{\mathbf{1.226 \times 10^{-9}}}{\sqrt{\text{V}}}\mathbf{m}$$

where V is potential in volts.

If an electron is accelerated through a potential of 1 kV *i.e.* 1000 V, its wavelength comes out to $[(1.226 \times 10^{-9}) \times (1000)^{-1/2}]$ 3.88×10^{-11} m or 38.8 pm. This wavelength is comparable to normal bond lengths in molecules. Therefore, the electrons accelerated in this way are used in the technique of *electron diffraction for the determination of molecular structure.*

Relationship between kinetic energy (K.E.) and wavelength (λ) of a moving particle.

$$\text{K.E.} = \frac{1}{2}mv^2$$

$$v^2 = \frac{2\,\text{K.E}}{\text{m}} \quad \text{or} \quad v = \sqrt{\frac{2\text{K.E}}{\text{m}}}$$

$$\text{Now} \qquad \lambda = \frac{h}{mv} = \frac{h}{m\sqrt{\frac{2\,\text{K.E}}{m}}}$$

$$\therefore \qquad \lambda = \frac{h}{\sqrt{2 \times \text{K.E.} \times m}}$$

Derivation of Bohr's Postulate of Quantisation of Angular Momentum from de-Broglie Relation

de-Broglie equation helped in explaining the Bohr's postulate regarding the quantisation of angular momentum of an electron. Consider an electron moving around the nucleus in the form of wave in a circular

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orbit of radius r. The wave train of electrons may be continuously *in phase* or *out of phase*. If the two ends of the wave meet to give a regular series of crests and troughs, the wave motion is said to be in phase as shown in Fig. 27 (a). If the two ends do not meet to give a regular series of crests and troughs, it is said to be out of phase [Fig. 27 (b)]. As evident from Fig. 25 (a), for wave motion to be continuously in phase, the circumference of circular orbit must be an integral multiple of number of the wavelengths otherwise the wave would interfere destructively and cancel each other and, thus, destroy itself. Therefore, by considering the electron as wave, we automatically impose a limit to the number of orbits.

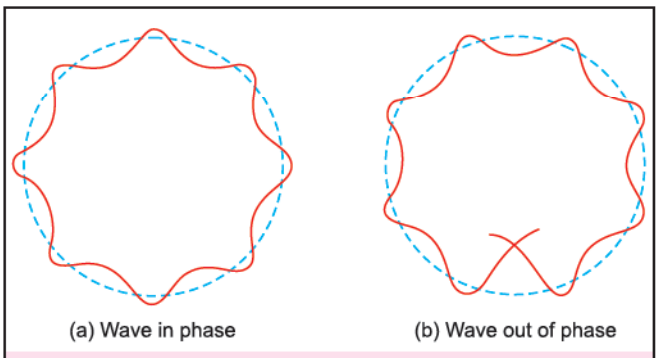

Fig. 27. Representation of electron waves and orbits (a) in phase (b) out of phase.

From the above discussion, it is clear that the circumference of the orbit must be integral multiple of the electron wavelength *i.e.*,

$$\text{Circumference} = n\lambda$$

or $$2\pi r = n\lambda$$

But, according to de-Broglie equation, $\lambda = \frac{h}{mv}$

$$\therefore \quad 2\pi r = \frac{nh}{mv}$$

or $$mvr = \frac{nh}{2\pi} \quad ...(iii)$$

Thus, the angular momentum of the electron should be an integral multiple of $h/2\pi$. In other words, the angular momentum is quantised. This is the same as Bohr's condition *for quantisation of angular momentum of fixed energy orbits.*

REMEMBER

Number of waves in *n*th orbit

$$= \frac{\text{Circumference of the orbit}}{\text{Wavelength}}$$

$$= \frac{2\pi r}{\lambda} = \frac{2\pi r}{h/mv} = \frac{2\pi\, mvr}{h}$$

$$= \frac{2\pi\left(\frac{nh}{2\pi}\right)}{h} = \boldsymbol{n}$$

Distinction between Electromagnetic Waves and Matter Waves

The important differences between electromagnetic waves and matter waves are given below :

Electromagnetic waves	Matter waves
1. Electromagnetic waves are associated with electric and magnetic fields perpendicular to each other and to the direction of propagation of radiation.	Matter waves may not be associated with electric and magnetic fields.
2. Electromagnetic waves can be radiated into space or emitted.	Matter waves are neither radiated into space nor emitted by the particles. These are simply associated with the particles.
3. They do not require any medium for propagation *i.e.*, these waves can pass through vacuum.	They require medium for propagation *i.e.*, these waves cannot pass through vacuum.
4. All electromagnetic waves travel with the same velocity.	Matter waves travel with different velocities.
5. The velocity of all electromagnetic waves is equal to that of light (3×10^8 m/s).	The velocity of matter waves is generally less than that of light.
6. The wavelengths of electromagnetic radiations are much large and are given by the relation, $\lambda = \frac{c}{\nu}$ where ν is the frequency.	The matter waves have shorter wavelengths given by de-Broglie equation, $\lambda = \frac{h}{mv}$

R.U. Curious...

❑ **Is electron really a particle or wave ?**

A question comes to our mind *"Is the electron really a particle or is it a wave ?" and "What does it look like ?"*

➤ Upto the year 1924, the electron was exclusively regarded as a particle. However, in 1924, de-Broglie suggested that the electron behaves both as a material particle and as a wave. Just like light, some experimental facts can be explained by assuming electrons as tiny particles while some other facts can be explained only on the basis of wave character of the electrons. Thus, the electron behaves as a particle as well as a wave.

The electrons are so small that they cannot be seen even with the help of a powerful microscope. But there is no doubt regarding their existence, rather they are the essential constituents of all forms of matter. Thus, they can be imagined to look like very tiny dots executing wave like motion and moving with speed 3×10^8 m/sec.

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SOLVED EXAMPLES

Example 29.

A tennis ball of mass 6.0×10^{-2} kg is moving with a speed of 62 m s^{-1}. Calculate the wavelength associated with this moving tennis ball. Will the movement of this ball exhibit a wave character ? Explain. ($h = 6.63 \times 10^{-34}$ kg m^2 s^{-1})

Solution : According to de-Broglie equation :

$$\lambda = \frac{h}{mv}$$

$m = 6.0 \times 10^{-2}$ kg,

$v = 62$ m s^{-1}, $h = 6.63 \times 10^{-34}$ kg m^2 s^{-1}

$$\therefore \quad \lambda = \frac{6.63 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{6.0 \times 10^{-2}\ \text{kg} \times 62\ \text{m s}^{-1}}$$

$$= \mathbf{1.8 \times 10^{-34}\ m}$$

This wavelength is too small to be measured and therefore, the wave nature of such a ball cannot be detected. Thus, the ball will not have wave character and will describe a fixed path.

Example 30.

Calculate de-Broglie wavelength of an electron (mass = 9.1 × 10 $^{-31}$ kg) moving at 1% speed of light. ($h = 6.63 \times 10^{-34}$ kg m^2 s^{-1})

Solution : We know that $\lambda = \frac{h}{mv}$

$m = 9.1 \times 10^{-31}$ kg, $h = 6.63 \times 10^{-34}$ kg m^2 s^{-1}

$$v = 1\% \text{ of speed of light} = \frac{1 \times 3.0 \times 10^8}{100}\ \text{m s}^{-1}$$

$= 3.0 \times 10^6$ m s^{-1} ($\because$ *speed of light* $= 3.0 \times 10^8$ *m* s^{-1})

$$\lambda = \frac{6.63 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{(9.1 \times 10^{-31}\ \text{kg}) \times (3.0 \times 10^6\ \text{m s}^{-1})} = \mathbf{2.43 \times 10^{-10}\ m.}$$

Example 31.

Calculate the wavelength of an electron moving with a velocity of 2.05×10^7 ms^{-1}. **N.C.E.R.T.**

Solution : According to de-Broglie wavelength,

$$\lambda = \frac{h}{mv}$$

$m = 9.11 \times 10^{-31}$ kg,

$h = 6.63 \times 10^{-34}$ kg $m^2 s^{-1}$,

$v = 2.05 \times 10^7$ m s^{-1}

$$\therefore \quad \lambda = \frac{6.63 \times 10^{-34}\ kg\ m^2\ s^{-1}}{(9.11 \times 10^{-31} kg) \times (2.05 \times 10^7 m\ s^{-1})}$$

$$= \mathbf{3.55 \times 10^{-11}\ m.}$$

Example 32.

Calculate the mass of a photon of sodium light having wavelength 5894 Å and velocity 3×10^8 m s^{-1}. ($h = 6.6 \times 10^{-34}$ kg m^2 s^{-1})

Solution : According to de-Broglie wavelength,

$$\lambda = \frac{h}{mv} \quad \text{or} \quad m = \frac{h}{\lambda v}$$

$\lambda = 5894$ Å $= 5894 \times 10^{-10}$ m,

$v = 3.0 \times 10^8$ m s^{-1},

$h = 6.6 \times 10^{-34}$ kg m^2 s^{-1},

$$\therefore \quad m = \frac{6.6 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{(5894 \times 10^{-10}\ \text{m}) \times (3.0 \times 10^8\ \text{m s}^{-1})}$$

$$= \mathbf{3.74 \times 10^{-36}\ kg}$$

Example 33.

A beam of helium atoms moves with a velocity of 2.0×10^3 ms^{-1}. Find the wavelength of the particle constituting the beam ($h = 6.626 \times 10^{-34}$ Js).

Solution :

$$\text{Mass of helium atom} = \frac{4}{6.022 \times 10^{23}}$$

$= 6.64 \times 10^{-24}$ g $= 6.64 \times 10^{-27}$ kg

According to de-Broglie equation,

$$\lambda = \frac{h}{mv}$$

$h = 6.626 \times 10^{-34}$ Js,

$m = 6.64 \times 10^{-27}$ kg

$v = 2.0 \times 10^3$ ms^{-1}

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{(6.64 \times 10^{-27}\ \text{kg}) \times (2.0 \times 10^3\ \text{ms}^{-1})}$$

$= 4.99 \times 10^{-11}$ m

$= 49.9$ pm

Example 34.

Two particles A and B are in motion. If the wavelength associated with the particle A is 5×10^{-8} m, calculate the wavelength of particle B if its momentum is half of A.

N.C.E.R.T. *(Pb. S.B. 2005)*

Solution : According to de-Broglie equation,

$$\lambda = \frac{h}{p}$$

For particle A : $\lambda_A = \frac{h}{p_A}$ ...(*i*)

For particle B : $\lambda_B = \frac{h}{p_B}$ ...(*ii*)

But $p_B = \frac{p_A}{2}$

$$\therefore \quad \lambda_B = \frac{h}{p_B} = \frac{h}{p_A/2} = \frac{2h}{p_A} \quad \text{... (iii)}$$

From equations (*i*) and (*iii*),

$$\frac{\lambda_A}{\lambda_B} = \frac{1}{2} \quad \text{or} \quad \lambda_B = 2\lambda_A$$

Now, $\lambda_A = 5 \times 10^{-8}$ m

$\therefore \quad \lambda_B = 2 \times 5 \times 10^{-8} = \mathbf{10^{-7}\ m.}$

Example 35.

If the velocity of electron in Bohr's first orbit is 2.19×10^6 ms^{-1}, calculate the de-Broglie wavelength associated with it. **N.C.E.R.T.**

Solution : According to de-Broglie equation

$$\lambda = \frac{h}{mv}$$

$m = 9.11 \times 10^{-31}$ kg,

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$v = 2.19 \times 10^6\ ms^{-1}$,

$h = 6.63 \times 10^{-34}\ kg\ m^2 s^{-1}$

$$\therefore \quad \lambda = \frac{6.63 \times 10^{-34}\ kg\ m^2 s^{-1}}{(9.11 \times 10^{-31}\ kg) \times (2.19 \times 10^6\ ms^{-1})}$$

$$= 3.32 \times 10^{-10}\ m = 332\ pm$$

❑ Example 36.

An electron is moving with a kinetic energy of 2.275×10^{-25} J. Calculate its de-Broglie wavelength. (Mass of electron = 9.1×10^{-31} kg, h = 6.6×10^{-34} J s)

Solution : Kinetic energy of electron,

$$\frac{1}{2}mv^2 = 2.275 \times 10^{-25}\ J \text{ or } = 2.275 \times 10^{-25}\ kg\ m^2\ s^{-2}$$

$$\text{or} \quad v^2 = \frac{2 \times 2.275 \times 10^{-25}}{m}$$

$$m = 9.1 \times 10^{-31}\ kg$$

$$v^2 = \frac{2 \times 2.275 \times 10^{-25}\ kg\ m^2\ s^{-2}}{9.1 \times 10^{-31} kg} = 0.5 \times 10^6\ m^2\ s^{-2}$$

$$v = 0.707 \times 10^3\ m\ s^{-1}$$

Now, $\lambda = \dfrac{h}{mv}$

$$\lambda = \frac{6.6 \times 10^{-34}\ kg\ m^2 s^{-1}}{(9.1 \times 10^{-31} kg) \times (0.707 \times 10^3\ m\ s^{-1})}$$

$$= 1.026 \times 10^{-6}\ m = \mathbf{1026\ nm}$$

❑ Example 37.

Calculate the kinetic energy of moving electron which has a wavelength of 4.8 pm. (mass of electron = 9.11×10^{-31} kg, h = 6.63×10^{-34} J s).

Solution : According to de-Broglie equation,

$$\lambda = \frac{h}{mv}$$

$h = 6.63 \times 10^{-34}$ J s,

$\lambda = 4.8$ pm $= 4.8 \times 10^{-12}$ m, $m = 9.11 \times 10^{-31}$ kg

$$4.8 \times 10^{-12} m = \frac{6.63 \times 10^{-34}\ kg\ m^2 s^{-1}}{9.11 \times 10^{-31} kg \times v}$$

$$\text{or} \quad v = \frac{6.63 \times 10^{-34}\ kg\ m^2 s^{-1}}{(4.8 \times 10^{-12} m) \times (9.11 \times 10^{-31} kg)}$$

$$= 1.516 \times 10^8\ m\ s^{-1}$$

$$\therefore \text{ Kinetic energy} = \frac{1}{2}mv^2$$

$$= \frac{1}{2} \times (9.11 \times 10^{-31}\ kg) \times (1.516 \times 10^8\ m\ s^{-1})^2$$

$$= 1.05 \times 10^{-14}\ kg\ m^2\ s^{-2}$$

$$\text{or} \quad = \mathbf{1.05 \times 10^{-14}\ J.}$$

❑ Example 38.

Calculate the wavelength of an electron that has been accelerated in a particle accelerator through a potential difference of 100 million volts. ($1\ eV = 1.6 \times 10^{-19}$ C, $m_e = 9.1 \times 10^{-31}$ kg, h = 6.6×10^{-34} Js) *(D.S.B. 2003)*

Solution : The kinetic energy of the electron under the potential difference of 100 million volts or 10^8 V is given by the relation :

$$\frac{1}{2}mv^2 = \text{eV}$$

$e = 1.6 \times 10^{-19}$ C, $V = 10^8$ V,

$m = 9.1 \times 10^{-31}$ kg

$$\frac{1}{2} \times 9.1 \times 10^{-31} \times v^2 = 1.6 \times 10^{-19}\ C \times 10^8\ V$$

$$\therefore \quad v^2 = \frac{2 \times 1.6 \times 10^{-19} \times 10^8}{9.1 \times 10^{-31}}$$

$$v^2 = 0.352 \times 10^{20}\ m^2\ s^{-2}$$

$$\text{or} \quad v = 5.93 \times 10^9\ m\ s^{-1}$$

Now, $\lambda = \dfrac{h}{mv}$

$$= \frac{6.6 \times 10^{-34}\ Js}{(9.1 \times 10^{-31} kg)(5.93 \times 10^9\ m\ s^{-1})}$$

$$= \mathbf{1.22 \times 10^{-13}\ m.}$$

❑ Example 39.

The mass of an electron is 9.1×10^{-31} kg. If its kinetic energy is 3.0×10^{-25} J, calculate its wavelength. **N.C.E.R.T.**

Solution : Kinetic energy, K.E. = $\dfrac{1}{2}mv^2$

$$\frac{1}{2}mv^2 = 3.0 \times 10^{-25}\ J = 3.0 \times 10^{-25}\ kg\ m^2\ s^{-2}$$

$$v^2 = \frac{2 \times 3.0 \times 10^{-25}\ kg\ m^2\ s^{-2}}{m} \quad (J = kg\ m^2\ s^{-2})$$

$$= \frac{2 \times 3.0 \times 10^{-25}\ kg\ m^2\ s^{-2}}{9.1 \times 10^{-31} kg}$$

$$\text{or} \quad v = \left(\frac{2 \times 3.0 \times 10^{-25}}{9.1 \times 10^{-31}}\right)^{1/2}\ m\ s^{-1} = 812\ m\ s^{-1}$$

Now, $\lambda = \dfrac{h}{mv}$

$$= \frac{6.626 \times 10^{-34}\ Js}{(9.1 \times 10^{-31} kg) \times (812\ m\ s^{-1})}$$

$$= 8967 \times 10^{-10}\ m = \mathbf{8967\ Å}$$

Practice Problems

34. What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 ms^{-1}. **N.C.E.R.T.**

35. Calculate the mass of a photon of light having wavelength 3.6 Å. **N.C.E.R.T.**

36. Calculate the momentum of a partcle which has a de-Broglie wavelength of 0.1 nm (h = 6.63×10^{-34} Js). **N.C.E.R.T.**

37. Calculate the kinetic energy of an α-particle which has a wavelength of 12 pm. **N.C.E.R.T.**

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38. The velocity associated with a proton moving is a potential difference of 1000 V is ms^{-1}. If the hockey ball of mass 0.1 kg is moving with the velocity, calculate the wavelength associated with this.

N.C.E.R.T.

39. What accelerating potential is needed to produce an electron beam with wavelength of 9 pm ?

N.C.E.R.T.

40. Calculate the de-Broglie wavelength of an electron that has been accelerated from rest through a potential difference of 1kV.

41. The kinetic energy of a subatomic particle is 5.85×10^{-25} J. Calculate the frequency of the particle wave.

42. What must be the velocity of a beam of electrons if they are to display a de-Broglie wavelength of 100 Å?

43. Calculate the wavelength associated with a moving electron having kinetic energy of 1.375×10^{-25} J. (mass of $e = 9.1 \times 10^{-31}$ kg, $h = 6.63 \times 10^{-34}$ kg $m^2 s^{-1}$).

Answers to Practice Problems

34. 6.626×10^{-34}m
35. 6.139×10^{-33} kg
36. 6.63×10^{-24} kg m s^{-1}
37. 2.30×10^{-19} J
38. 1.52×10^{-38} m
39. 1.86×10^{4} V
40. 3.88×10^{-11} m
41. 1.76×10^{9} s^{-1}
42. 7.28×10^{4} ms^{-1}
43. 1.32×10^{-6} m

Hints & Solutions on page 68

2. Heisenberg's Uncertainty principle

So far, we have been believing that anything can be specified to any desired degree of accuracy. However, Heisenberg in 1927, put forward a principle known as **Heisenberg's uncertainty principle.** It states that

it is not possible to measure simultaneously both the position and momentum (or velocity) of a microscopic particle, with absolute accuracy.

Mathematically, this law may be expressed as :

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

where Δx = uncertainty in position

Δp = uncertainty in momentum

The sign $\geq$ means that the product of Δx and Δp can be either greater than or equal to $h/4\pi$. It can never be less than $h/4\pi$. The sign of equality refers to minimum uncertainty and is equal to $h/4\pi$.

The constancy of the product of uncertainties means that :

(*i*) If Δx *is small i.e.,* the position of the particle is measured accurately, Δp *would be large, i.e.,* there would be large uncertainty in its momentum.

(*ii*) On the other hand, if Δp *is small,* the momentum of the particle is measured more accurately, Δx *would be large i.e.,* there would be large uncertainty with regard to the position of the particle.

In other words, *if the position of a particle is measured accurately, there will be more error in the measurement of momentum. Conversely, if momentum is measured more accurately, the position will not be accurately known.*

Since momentum $p = mv$, therefore, $\Delta p = m\Delta v$ because mass is constant. The above relation may also be written as :

$$\Delta x \times m(\Delta v) \geq \frac{h}{4\pi}$$

or $$\Delta x \times \Delta v \geq \frac{h}{4\pi m}$$

This also means that **the position and velocity of an object cannot be simultaneously known with accuracy.**

Physical concept of uncertainty principle. In order to understand the physical concept of uncertainty principle, let us study as to how the position of a material object is determined. To determine the position of an object, we must be able to see the object. This can be done with the help of light of suitable wavelength. When a beam of light falls on an object, the photons of this incident light are scattered at the object and the reflected light enters our eye. Now, if the object is large, its position and velocity will not change by the impact of the striking photons. Thus, it will be possible to determine both the position and velocity of the object simultaneously.

However, in case of microscopic objects, such as electrons, the interaction of the striking photon of light with the particle will cause appreciable displacement of the particle from its normal path. As a result of this, the particle undergoes a considerable change in its path and velocity (or momentum) due to the impact of a single photon used to observe it. Thus, the very act of measuring the position of the microscopic particle causes a change in its momentum. Fig. 28 shows as to how the position of an electron changes by the impact of photon. The collision of photon with the electron sends it in an unpredictable direction.

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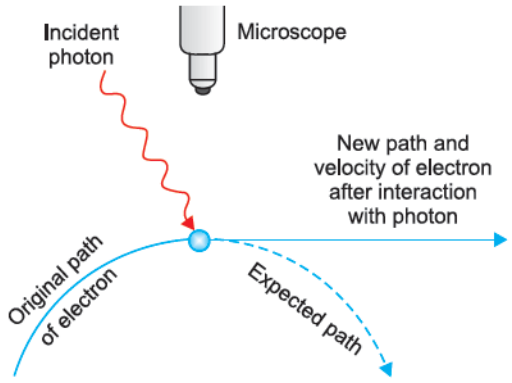

Fig. 28. The change in the path of electron by the impact of striking photon.

Thus, it is not possible to determine simultaneously the exact position and momentum of the electron or of any other microscopic object.

Let us consider a thought experiment for determining the position of an electron by using photons of light. According to principles of optics, if we use light of wavelength λ, then the position of electron cannot be located more accurately than $\pm\lambda$. The shorter the wavelength, the greater is the accuracy. Therefore, to observe the position of the electron accurately, light of appropriately small wavelength should be used. But the photons of radiations of smaller wavelength will have higher momentum ($p = h/\lambda$). When even a single photon of this light used to observe the position of electron strikes against it, a large amount of momentum will be transferred to the electron at the time of collision. This will change the velocity of the electron and consequently will result into greater uncertainty in velocity or momentum.

On the other hand, in order to minimise the change in momentum we have to use light having photons with small values of p. This will require radiations of longer wavelengths ($\lambda = h/p$). Now, if we use photons of light having larger wavelengths (low momentum), the velocity or momentum will not change appreciably but we will not be able to measure position accurately with larger wavelength. Therefore, uncertainty in position will increase. Thus, we cannot simultaneously measure the position and momentum of a small moving object like electron accurately.

Significance of Uncertainty Principle in Our Daily Life

One of the important implications of the Heisenberg's uncertainty principle is that it rules out the well defined circular paths (orbits) or trajectories proposed by Bohr. Since for a subatomic particle like an electron, it is not possible to simultaneously determine the position and velocity at any moment with good degree of precision, therefore, it is not possible to talk about the trajectory of an electron or well defined circular orbits.

It should be borne in mind that the uncertainty is not due to lack of sufficiently refined techniques but it is due to the fact that we cannot observe microscopic things without disturbing them. No instrument can observe the position of an electron without affecting its motion. In other words, uncertainty principle is the **fundamental limitation of nature.** Thus, we cannot design an experiment to obtain an accurate value of both the position and momentum for microscopic objects.

However, in our daily life, this principle has no significance. This is because we come across only large objects, i.e., the objects which we can observe with naked eye without altering their motion. The position and velocity of these objects can be determined accurately because in these cases, during the interaction between the object and the measuring device, the changes in **position** and **velocity are negligible.**

This may also be illustrated as follows :

If uncertainty principle is applied to a microscopic object like an electron, $\Delta x \times \Delta v$ comes out to be of the order of 10^{-5} m^2 s^{-1} as :

$$\Delta x \times \Delta v = \frac{h}{4\pi m}$$

$$= \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.1416 \times 9.11 \times 10^{-31} \text{ kg}}$$

$$= 5.78 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$$

It also means that if one tries to find the exact position of the electron, say to an uncertainty of about 1Å (1×10^{-8} m), then uncertainty in velocity, Δv would be

$$\Delta v = \frac{5.78 \times 10^{-5}}{10^{-8}} = 5.78 \times 10^{3} \text{ ms}^{-1}$$

This is very large. On the other hand, if uncertainty principle is applied to an object of mass say about a milligram (10^{-6} kg), then

$$\Delta x \times \Delta v = \frac{h}{4\pi m}$$

$$= \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.1416 \times 10^{-6} \text{ kg}}$$

$$= 5.27 \times 10^{-29} \text{ m}^2 \text{s}^{-1}$$

The value of $\Delta x . \Delta v$ for milligram sized or heavier objects is extremely small. Therefore, uncertainty of such small values have no significance.

SOLVED EXAMPLES

❑ **Example 40.**

Calculate the uncertainty in the position of an electron if the uncertainty in its velocity is

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5.7×10^5 m s^{-1}. ($h = 6.6 \times 10^{-34}$ J s and mass of electron = 9.1×10^{-31} kg)

Solution : According to Heisenberg's uncertainty principle,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \times m\Delta v \geq \frac{h}{4\pi}$$

$$\therefore \Delta x \geq \frac{h}{4\pi m \Delta v}$$

$\Delta v = 5.7 \times 10^5$ m s^{-1}, $m = 9.1 \times 10^{-31}$ kg,

$h = 6.6 \times 10^{-34}$ J s

$$\therefore \Delta x = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.142 \times (9.1 \times 10^{-31} \text{ kg}) \times (5.7 \times 10^5 \text{ m s}^{-1})}$$

$$= \mathbf{1.012 \times 10^{-10} \text{ m}}.$$

❑ Example 41.

Calculate the uncertainty in the velocity of a wagon of mass 2000 kg whose position is known to an accuracy of ± 10 m. **N.C.E.R.T.**

Solution : Mass of wagon = 2000 kg

Uncertainty in position, $\Delta x = \pm 10$ m

According to Heisenberg uncertainty principle

$$\Delta x \times \Delta p = \frac{h}{4\pi} \quad \text{or} \quad \Delta x \times \Delta v = \frac{h}{4\pi m}$$

$$\text{or} \quad \Delta v = \frac{h}{4\pi m \Delta x}$$

$$= \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.1416 \times (2000 \text{ kg}) \times (10 \text{ m})}$$

$$= \mathbf{2.636 \times 10^{-39} \text{ m s}^{-1}}.$$

❑ Example 42.

On the basis of Heisenberg uncertainty principle, show that electron cannot exist within the atomic nucleus of radius 10^{-15}m.

Solution : The radius of the atomic nucleus is 10^{-15} m. Now, if the electron were to exist within the nucleus, then the maximum uncertainty in its position would have been 10^{-15} m.

$$\text{or} \quad \Delta x = 10^{-15} \text{ m}$$

Now according to uncertainty principle,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

$$\text{or} \quad \Delta x \times m\Delta v \geq \frac{h}{4\pi}$$

$$\text{or} \quad \Delta v \geq \frac{h}{4\pi m \Delta x}$$

Mass of electron, $m = 9.1 \times 10^{-31}$ kg,

$\Delta x = 1 \times 10^{-15}$ m

$$\therefore \Delta v = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 1 \times 10^{-15}}$$

$$= \mathbf{5.77 \times 10^{10} \text{ m s}^{-1}}.$$

The value of uncertainty in velocity, Δv is much higher than the velocity of light (3.0×10^8 m s^{-1}) and therefore, it is not possible. Hence an electron cannot be found within the atomic nucleus.

❑ Example 43.

Calculate the uncertainty in the position of an electron if uncertainty in its velocity is (i) 0.001% (ii) zero.

(The mass of electron = 9.1×10^{-31} kg, velocity of electron = 300 m s^{-1}).

Solution : Mass of electron = 9.1×10^{-31} kg,

$h = 6.6 \times 10^{-34}$ J s

(*i*) When Δv = 0.001% of velocity of electron

$$= \frac{0.001 \times 300}{100} = 3.0 \times 10^{-3} \text{ m s}^{-1}$$

Now, $\Delta x \times m\,\Delta v = \frac{h}{4\pi}$

$$\therefore \Delta x = \frac{h}{4\pi m \Delta v}$$

$$= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.142 \times (9.1 \times 10^{-31} \text{ kg}) \times (3.0 \times 10^{-3})}$$

$$= \mathbf{1.92 \times 10^{-2} \text{ m}}.$$

(*ii*) When $\Delta v = 0$

$$\Delta x = \frac{h}{4\pi m \Delta v}$$

If Δv is zero, then denominator in the above expression becomes zero and, therefore, uncertainty in position is **infinity.**

❑ Example 44.

An electron has a speed of 500 m s^{-1} with uncertainty of 0.02%. What is the uncertainty in locating its position ?

Solution : Velocity of electron = 500 m s^{-1}

Uncertainty in velocity, $\Delta v = 500 \times 0.02\%$

$$= \frac{500 \times 0.02}{100}$$

$$= 0.1 \text{ m s}^{-1}$$

Mass of electron, $m = 9.1 \times 10^{-31}$ kg

$h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}

According to uncertainty principle, $\Delta x \times \Delta p \geq \frac{h}{4\pi}$

$$\text{or} \quad \Delta x \times m\,\Delta v \geq \frac{h}{4\pi}$$

$$\text{or} \quad \Delta x \geq \frac{h}{4\pi m \Delta v}$$

$$\geq \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{s}^{-1}}{4 \times \frac{22}{7} \times 9.1 \times 10^{-31} \times 0.1}$$

$$\geq \mathbf{5.77 \times 10^{-4} \text{ m}}$$

$\therefore$ Uncertainty in position $= \mathbf{5.77 \times 10^{-4} \text{ m}}$.

❑ Example 45.

A golf ball has a mass of 40 g and a speed of 45 m/s. If the speed can be measured with accuracy of 2%, calculate the uncertainty in position. **N.C.E.R.T.**

Solution : The uncertainty in speed,

$$\Delta v = 45 \times \frac{2}{100} = 0.9 \text{ ms}^{-1}$$

$$m = 40 \times 10^{-3} \text{ kg}$$

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$$\Delta x = \frac{h}{4\pi m \Delta v}$$

$$= \frac{6.626 \times 10^{-34} \text{kg m}^2 s^{-1}}{4 \times 3.14 \times 40 \times 10^{-3} \text{kg} \times 0.9 \text{ ms}^{-1}}$$

$$= \mathbf{1.46 \times 10^{-33} m}$$

❑ **Example 46.**

If the position of the electron is measured within an accuracy of ± 0.002 nm, calculate the uncertainty in the momentum of the electron. If suppose the momentum of the electron is

$$\frac{h}{4\pi m} \times 0.05 \text{ nm},$$

is there any problem in defining this value?

N.C.E.R.T.

Solution : According to uncertainty principle,

$$\Delta x \times \Delta p = \frac{h}{4\pi}$$

$$\Delta x = \pm 0.002 \text{ nm} = \pm 0.002 \times 10^{-9} \text{ m}$$

$$\Delta p = \frac{h}{4\pi \Delta x} = \frac{6.626 \times 10^{-34} kg\ m^2 s^{-1}}{4 \times \frac{22}{7} \times 0.002 \times 10^{-9} \text{ms}^{-1}}$$

$$= 2.63 \times 10^{-23} kg\ m\ s^{-1}.$$

Uncertainty in momentum is $\frac{h}{4\pi m} \cdot \frac{1}{0.002 \times 10^{-9}} = \frac{h}{4\pi m} \cdot 5 \times 10^{11}$ which is much larger than actual momentum *i.e.*, $\frac{h}{4\pi m} \times 0.05$ nm, therefore, it cannot be defined.

Practice Problems

44. A microscope using suitable photons is employed to locate an electron in atom within a distance of 0.1 Å. What is the uncertainty involved in the measurement of its velocity ? (mass of electron = 9.11×10^{-31} kg, $h = 6.626 \times 10^{-34}$ Js) **N.C.E.R.T.**

45. Table-tennis ball has a mass 10 g and speed of 90 ms^{-1}. If speed can be measured within an accuracy of 4%, what will be the uncertainty in speed and position.

46. Calculate the minimum uncertainty in velocity of a particle of mass 1.1×10^{-27} kg if uncertainty in its position is 3×10^{-10} cm ($h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}).

47. The uncertainties in the position and velocity of a particle are : 10^{-10} m and 5.27×10^{-24} m s^{-1}. Calculate the mass of particle ($h = 6.626 \times 10^{-34}$ J s).

48. A proton is accelerated to one-tenth of the velocity of light. If its velocity can be measured with a precision of ± 1%, what must be its uncertainty in position ? ($h = 6.6 \times 10^{-34}$ J s, mass of proton = 1.66×10^{-27} kg).

49. A proton is accelerated to a velocity of 3×10^7 ms^{-1}. If the velocity can be measured with a precision of ±0.5%, calculate the uncertainty in position of proton. ($h = 6.6 \times 10^{-34}$ Js, mass of proton = 1.66×10^{-27}kg)

Answers to Practice Problems

44. 5.79×10^6 ms^{-1}.
45. 3.6 m s^{-1}, 1.46×10^{-33} m.
46. 1.59×10^4 m s^{-1}.
47. 0.10 kg.
48. 1.06×10^{-13} m.
49. 2.11×10^{-13} m.

Hints & Solutions on page 68

QUANTUM MECHANICAL MODEL OF ATOM AND CONCEPT OF ATOMIC ORBITAL

The wave character of an electron and uncertainty in its position and momentum gave a serious blow to Bohr's model of an atom. According to Bohr, the electrons revolve around the nucleus in certain well defined circular orbits. **But the idea of uncertainty in position and velocity overruled the Bohr's picture of fixed orbits**. Thus, the classical mechanics could not describe the behaviour of electrons in atoms correctly. Therefore, the scientists started looking for a model which could incorporate the dual character of matter and uncertainty principle. This resulted in a new approach called **quantum mechanics** or **wave mechanics.**

Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrodinger. On the basis of quantum mechanics, Schrodinger proposed a model of an atom which considered wave-particle duality of matter and Heisenberg uncertainty principle. This model was known as **quantum mechanical model of atom.** In 1927, Erwin Schrodinger described the wave motion of the electron in three dimensional space around the nucleus by a mathematical equation known as **Schrodinger wave equation.**

The Schrodinger wave equation is :

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

where ψ is the amplitude of the wave, x, y and z are the coordinates of the position of electron, E is the total energy of the electron, V is the potential energy, m is the mass of the electron and h is the Planck's constant. $\delta^2\psi/\delta x^2$ represents second differential derivative of ψ w.r.t. x, $\delta^2\psi/\delta y^2$ represents second differential derivative of ψ w.r.t. y and $\delta^2\psi/\delta z^2$ represents second differential derivative of Ψ w.r.t. z. In short, the Schrodinger wave equation may be written as :

$$\hat{H}\Psi = E\Psi$$

where $\hat{H}$ is a mathematical operator called **Hamiltonian operator.** The solutions of Schrodinger wave equations give E and Ψ.

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Although the Schrodinger wave equation was difficult to accept at first, it has now gained wide acceptance. This is because the results obtained from Schrodinger wave equation are in excellent agreement with the experimental findings. One of the major achievement of Schrodinger wave equation is that it successfully interpreted the experimental information about atoms and molecules.

KEY NOTE

Operators

While studying the state of a system, we make various measurements of its properties such as mass, volume, momentum, position and energy. Each individual property is called **observable.** In order to determine the value of the observable property, we have to perform certain mathematical operations. This operation is represented by an **operator.** Therefore, **operator is a mathematical command or instruction which acts on a mathematical function.** For example, in the equation $4 \times 5 = 20$, the operation is multiplication and the operator is '×'. We can also express the multiplication operation with some symbols, designated as $\hat{M}$. For example, $\hat{M}(4 \times 5) = 20$. In this case, $\hat{M}$ is multiplication operator, where the ^ signifies an operator.

Schrodinger Wave Equation for Hydrogen Atom

● When Schrodinger wave equation was solved for hydrogen atom, the solution gives the possible energy states (or energy levels) that an electron can occupy. These values of energy are called **eigen values.** The corresponding values of wave functions (Ψ) of the electron associated with these energy values are called **eigen functions**.

● The wave functions and the corresponding energy states are characterized by a set of three quantum numbers (principal quantum number n, azimuthal quantum number l and magnetic quantum number m_l). These numbers arise as a natural consequence in the solution of the Schrodinger wave equation. This quantum mechanical model of the hydrogen atom successfully predicts all aspects of hydrogen atom spectrum and other phenomena which could not be explained by Bohr model.

● The Schrodinger wave equation cannot be solved exactly for multielectron atoms. However, approximate methods can be used to get solutions of reasonable accuracy.

Physical significance of wave function.

In the physical sense, ψ gives the *amplitude of the wave associated* with the electron. We know that in the case of light waves, the square of the amplitude of the wave at a point is proportional to the intensity of light. Extending the same concept to electron wave motion, the square of the wave function, ψ^2 may be taken as *intensity of electron at any point.* In other words, ψ^2 determines the probability of finding the moving electron in a given region *i.e.* it gives the probability density. Thus, ψ^2 has been called the **probability density** and **ψ the probability amplitude.** Hence, the solutions of Schrodinger wave equation replace the discrete energy levels or orbits proposed by Bohr and led to the concept of *most probable regions in space* in terms of ψ^2. A large value of ψ^2 means a high probability of finding the electron at that place and a small value of ψ^2 means low probability. If ψ^2 is almost zero at a particular point, it means that the probability of finding the electron at that point is negligible.

Energy of electron in an atom

When the Schrodinger wave equation was solved for hydrogen atom, it gave the following expression for the energy of electron :

$$E_n = -\frac{2\pi^2 m_e e^4}{n^2 h^2}$$

The above expression is same as Bohr's equation for the energy of electron in a hydrogen atom. Substituting the values of m_e, and h, the above expression becomes :

$$E_n = -\frac{2.18 \times 10^{-18}}{n^2} \text{ J per atom}$$

$$\text{or} \quad = -\frac{1.312 \times 10^{6}}{n^2} \text{ J per mol}$$

Important Features of the Quantum Mechanical Model of Atom

The important features of the quantum mechanical model of an atom are summed up below :

1. The energy of electrons in atoms is **quantized** *i.e.*, they can have only certain specific values.

2. The existence of quantized electronic energy levels is a direct result of the wave like properties of electrons and are the allowed solutions of Schrodinger equation.

3. This gives the most probable regions in an atom where the probability of finding the electrons is maximum. Therefore, this model is in accordance with the Heisenberg uncertainty principle and does not specify the exact position and momentum of the electron. But it talks about the most probable regions called **orbitals**.

4. An atomic orbital is described with the help of wave function ψ for an electron in an atom. Whenever, an electron is described by a wave function, we say that the electron occupies that orbital. Therefore, the

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wave functions for an electron in an atom are also called **orbital wave functions** or simply **atomic orbitals.** Since many wave functions are possible for an electron, there are many atomic orbitals in an atom. In each orbital, an electron has definite energy. Thus, all the information about the electron in an atom is provided by its orbital wave function ψ.

5. The probability of finding the electron at a point within an atom is proportional to the square of the wave function *i.e.*, $|\psi|^2$ at that point. Therefore, $|\psi|^2$ is known as **probability density** and is always positive.

6. The probability of finding the electron in a region having volume dV can be obtained as $\psi^2 . dV$, where dV is the infinitesimally small volume $(dx . dy . dz)$.

7. The quantum mechanical model gave three constants, known as quantum numbers which are required to specify the position and energy of the electron in an atom. These are discussed later.

Probability Picture of an Electron : Concept of atomic orbital.

The solution of Schrodinger wave equation led to the concept of ***most probable regions*** in place of well-defined circular paths proposed by Bohr. According to this approach, we cannot say simply that the electron exists at a particular point, but we talk about certain regions in space around the nucleus where the probability (chances) of finding the electron is maximum (90–95%). These most probable regions in space are called **orbitals.** Thus,

an orbital may be defined ***as a region in space around the nucleus where the probability of finding the electron is maximum.***

If a boundary is drawn which encloses a region where there is high probability (90–95%) of finding the electron, the figure obtained, gives the general picture of orbital. For the sake of simplicity, it may be drawn as shown in Fig. 29 (*a*). The orbital, here is shown by dotted figure representing electron cloud. The intensity of dots gives the relative probability of finding the electron in that particular region. It may be noted that there are some chances of finding the electron even outside the figure. Fig. 29 provides a comparison of an orbital with the circular orbit proposed by Bohr.

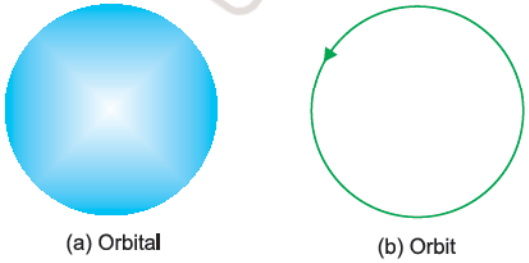

Fig. 29. (*a*) Electron cloud representation of an orbital (*b*) Bohr's orbit.

Differences between Orbit and Orbital

The main differences between orbit and orbital are summed up below :

Orbit	Orbital
1. Orbit is a well-defined circular path around the nucleus in which an electron revolves.	1. It represents the region in space around the nucleus in which the probability of finding the electron is maximum.
2. It represents the planar motion of an electron.	2. It represents the three-dimensional motion of an electron around the nucleus.
3. Orbit gives a definite path of an electron and this concept is not in accordance with the uncertainty principle.	3. Orbital does not specify definite path and according to this concept, electron may be any-where in this region. This concept is in accordance with the uncertainty principle.
4. All orbits are circular.	4. Orbitals have different shapes. For example, *s*-orbital is spherical, while *p*-orbital is dumb bell shaped.
5. Orbits do not have directional characteristics.	5. Except *s*-orbitals, all other orbitals have directional characteristics.
6. An orbit can accommodate electrons equal to $2n^2$ where n represents the principal quantum number.	6. An orbital cannot accommodate more than two electrons.

QUANTUM NUMBERS

As discussed earlier, orbitals represent regions in space around the nucleus where the probability of finding the electron is maximum. A large number of electron orbitals are possible in atom. These can be distinguished by their size, shape and orientation.

To describe each electron in an atom in different orbitals, we need a set of three numbers known as quantum numbers. These are designated as n, l and m_l. In addition to these, three numbers another quantum number is also needed which specifies the spin of the electron. These four numbers are called **quantum numbers.** These are discussed below :

1. Principal quantum number (n). This quantum number *determines the main energy shell or level in which the electron is present.* It is denoted by n. It can have whole number values starting from 1 such as

$$n = 1, 2, 3, 4 ....$$

This quantum number also identifies as **shell.** The shell with $n = 1$ is called the *first shell*. The shell with $n = 2$ is called the second shell and so on. The various shells are also called K, L, M, N as :

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n	1	2	3	4 ...
shell	K	L	M	N ....

The principal quantum number gives the following informations:

(*i*) *It gives the average distance of the electron from the nucleus.* If $n = 1$ (first shell), it is closest to the nucleus and has lowest energy. As the value of n increases, the distance of the electron from the nucleus increases.

(*ii*) *It determines the energy of the electron,* according to the formula,

$$E_n = -\frac{2\pi^2 me^4}{n^2h^2}$$

$$= -\frac{1311.8}{n^2} \text{ kJ mol}^{-1}$$

For example, the energy of electron in K-shell ($n = 1$), is

$$E_1 = -\frac{1311.8}{1^2} = -1311.8 \text{ kJ mol}^{-1}$$

Similarly, the energy of the electron in L shell ($n = 2$), E_2, M-shell ($n = 3$), E_3..... are respectively,

$E_2 = -327.9$ kJ mol^{-1} $E_3 = -145.7$ kJ mol^{-1}

Thus, *principal quantum number gives the average distance of the electron from the nucleus (size of electron cloud or shell) and energy associated with it.*

2. Azimuthal quantum number (*l*). This quantum number determines the angular momentum of the electron. This quantum number is also known as **orbital angular momentum** or **subsidiary quantum number.**

This is denoted by l. The value of l gives the **subshell** or **sublevel** in a given principal energy shell to which an electron belongs. It can have positive integer values ranging from zero to $(n-1)$ where n is the principal quantum number. That is,

$$l = 0, 1, 2, 3 \ldots (n-1)$$

The azimuthal quantum number gives the following **informations:**

(*i*) *It gives the number of subshells present in a principal shell.* The value of 'l' depends upon the value of n.

For example, for $n = 1$, l has only one value: $l = 0$ *i.e.*, one subshell

For $n = 2$, l has two values : $l = 0, 1$ *i.e.*, two subshells.

For $n = 3$, l has three values : $l = 0, 1, 2$ *i.e.*, three subshells.

Thus, for each value of n, there are n possible values of l. In other words, *the number of subshells in a principal shell is equal to the value of n.*

The various subshells or values of l are also designated by letters s, p, d, f ... as

Value of *l*	0	1	2	3	4	5 ...
Designation	*s*	*p*	*d*	*f*	*g*	*h* ...

The letters s, p, d and f originate from the terms sharp, principal, diffuse and fundamental, which were used in the atomic emission spectra. For $l = 4$ and higher values, the letters follow alphabetical order after f, *i.e.*, $l = 4$ is designated as g; $l = 5$ is designated as h and so on.

Thus, for $n = 1$, $l = 0$

This means that the first principal energy level consists of only one sublevel termed as s.

Similarly, for $n = 2$, $l = 0$, 1 *i.e.*, the second principal energy level consists of two sublevels, s ($l = 0$) and p ($l = 1$).

For $n = 3$, $l = 0$, 1, 2 *i.e.*, third principal energy level consists of three sublevels s ($l = 0$), p ($l = 1$) and d ($l = 2$).

The different subshells or sublevels are represented by first writing the value of n (1, 2, 3...) and then the letter designation for the value of l (s, p, d, f...). For example, an orbital with $n = 1$ and $l = 0$ is denoted as 1s, an orbital with $n = 3$, $l = 2$ is denoted as 3d. The designations of subshells for $n = 1$ to $n = 4$ are given below :

n	*l*	Subshell designation	No. of subshells in a shell
1	0	1s	One
2	0	2s	Two
	1	2p	
3	0	3s	Three
	1	3p	
	2	3d	
4	0	4s	Four
	1	4p	
	2	4d	
	3	4f	

(*ii*) *It gives the relative energies of various shells.*

Except for hydrogen, the subshells within a given shell differ slightly in energy. The energy of a subshell increases with increasing value of l. This means that within a given shell, the s-subshell ($l = 0$) has lowest energy, p-subshell ($l = 1$) has next to lowest, followed by d, then f and so on. For example, in fourth energy shell, the energies of subshell increases as :

$$4s < 4p < 4d < 4f$$

Increasing energy

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(iii) This quantum number gives the energy of the electron due to the angular momentum of the electron. The angular momentum of the electron is related to l as :

$$\text{Angular momentum} = \frac{h}{2\pi}\sqrt{l(l+1)}$$

KEY NOTE

- Some books express angular momentum as :

  $\text{Angular momentum} = \sqrt{l\,(l+1)}\,\hbar$

  The use of $\hbar$ is a shorthand way of writing $h/2\pi$ and is extensively used in Quantum mechanics.
- It may be noted that angular momentum depends only on the value of l and not on the value of n. This means that 1*s*, 2*s*, 3*s*, etc. electrons will have same angular momentum. Similarly, all *p*-electrons or *d*-electrons or *f*-electrons will have same angular momentum.

Thus, *azimuthal quantum number determines the subshell in a given principal shell, angular momentum of the electron present in the subshell and relative energies of various subshells.*

3. Magnetic quantum number (m_l). This quantum number describes the behaviour of electron in a magnetic field. We know that the movement of electrical charge is always associated with magnetic field. Since the revolving electron possesses angular momentum, it will give rise to a very small magnetic field which will interact with the external magnetic field of the earth. Under the influence of external magnetic field, the electrons in a given subshell orient themselves in certain preferred regions of space around the nucleus. These are called **orbitals.** Thus, this quantum number gives the number of orbitals in a given subshell. It is designated by m_l. The allowed values of m_l depends upon the value of l. For a given value of l, m can have values $-l$ through 0 to $+l$. That is

$$m_l = -l \ldots\ldots 0 \ldots\ldots +l$$

In other words, there are $(2l + 1)$ values of m for each value of l.

This quantum number gives the number of orbitals in a subshell. For example,

If $l = 0$, m has only one value, *i.e.*, $m_l = 0$

i.e., *s* subshell has only one orbital called ***s*-orbital.**

If $l = 1$, m_l may be $-1, 0, +1$.

i.e., ***p*-subshell** contains three orbitals called ***p*-orbitals.** These are indicated by numerical subscripts (p_{+1}, p_0, p_{-1}) or these are designated by alphabetical subscripts (p_x, p_y and p_z). Thus, there are three 2*p*-orbitals, designated as $2p_x$, $2p_y$ and $2p_z$.

NOTE

Some books use different values of m for p_x, p_y and p_z orbitals. However, it may be noted that for a p_z-orbital, the value of m has been **conventionally** taken to be equal to zero, *i.e.*, $m = 0$. But a p_x or a p_y-orbital does not designate only one value of m but a linear combination of orbitals with $m = +1$ and $m = -1$. Therefore, it is not correct to designate single value of m for a p_x orbital as +1 or −1.

If $l = 2$, m_l may be $-2, -1, 0, +1, +2$.

***i.e.*, *d*-subshell** contains five orbitals called ***d*-orbitals.**

Similarly,

if $l = 3$, m_l may be $-3, -2, -1, 0, +1, +2, +3$.

i.e., ***f*-subshell** contains seven orbitals called ***f*-orbitals.**

The number of orbitals in a given subshell are given below :

Subshell	*s*	*p*	*d*	*f*	*g*
No. of orbitals	1	3	5	7	9

It can be generalised that there are **$(2l + 1)$** orbitals (or m values) for each value of l (or subshell).

By working out different combinations of these quantum numbers, it can be easily calculated that there is *one* orbital for $n = 1$ (1*s*), *four* for $n = 2$ (2*s* and three 2*p*), *nine* for $n = 3$ (3*s*, three 3*p*, five 3*d*). These are given above in Table 4.

Thus, *magnetic quantum number determines the number of orbitals present in a given subshell.*

Table 4. Permitted combinations of n, l and m_l.

Value of n	Value of l	Value of m_l	Subshell	No. of orbitals	
1	0	0	1*s*	1	
2	0	0	2*s*	1	= 4
	1	−1, 0, +1	2*p*	3	
3	0	0	3*s*	1	= 9
	1	−1, 0, +1	3*p*	3	
	2	−2, −1, 0, +1, +2	3*d*	5	

4. Spin quantum number(m_s). It is observed that the electron in an atom is not only revolving around the nucleus but is also spinning around its own axis. *In 1925, George Uhlenbeck and Samuel* Goudsmit *proposed fourth quantum number known as* ***electron spin quantum*** *number. This quantum number describes the spin orientation of the electron.* It is designated by m_s. Since the electron can spin in only two ways—clockwise or anti-clockwise and, therefore, the spin quantum number can take only two values : $+\frac{1}{2}$ or $-\frac{1}{2}$. This quantum number has a value independent of the values of the other three quantum numbers. Instead of giving number for $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$ the two orientations are usually designated by arrows pointing up and down : ↑ (spin up) or ↓ (spin down) respectively.

Thus, an electron has also spin angular momentum commonly called spin. The magnitude of spin angular momentum of an electron is given as :

$$\text{Spin angular momentum} = \sqrt{s(s+1)}\,\frac{h}{2\pi}$$

For example, for spin quantum number, $s = \frac{1}{2}$

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Spin angular momentum = $\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\frac{h}{2\pi} = \frac{\sqrt{3}h}{4\pi}$

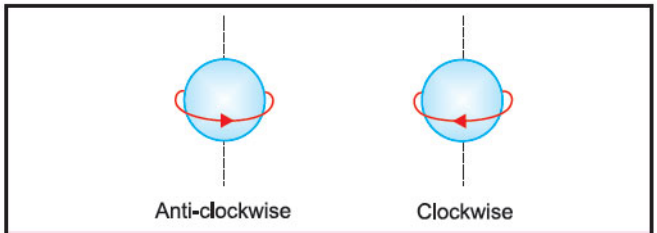

Fig. 30. Two possible orientations of the spin of an electron $m_s = +½$ and $m_s = -½$

To **sum up** the four quantum numbers provide the following informations about orbitals :

1. n describes the **shell**, determines the size of the orbital and also to the large extent the energy of the orbital.

2. l determines the **subshell** and shape of the orbital. There are n subshells in nth shell. To some extent, l also determines the energy of the orbital in a multi-electron atom.

3. m_l designates the **orientation** of the **orbital.** For a given value of l, m_l can have $(2l + 1)$ values or number of orbitals. For example, one s-orbital ($l = 0$), three p-orbitals ($l = 1$), five d-orbitals ($l = 2$) per subshell.

4. m_s refers to the orientation of the spin of the electron.

Thus, the four quantum numbers describe the position of an electron in an atom by specifying its main ***shell*** (n), ***subshell*** (l), the orientation of the ***orbital*** (m_l) and **direction of its spin** (m_s). In other words, *these quantum numbers serve as an address for an electron.*

The various permitted values of the quantum numbers are summarized below.

Name	Symbol	Information provided	Permitted values
Principal	n	shell	1, 2, 3, 4...
Azimuthal	l	subshell	0, 1, 2, 3 ... $(n-1)$
Magnetic	m_l	orbital	$-l$ ... 0 ... $+l$
Spin	m_s	spin	$+½, -½$

The number of subshells and orbitals in first three shells (K, L and M) are shown in Fig. 31.

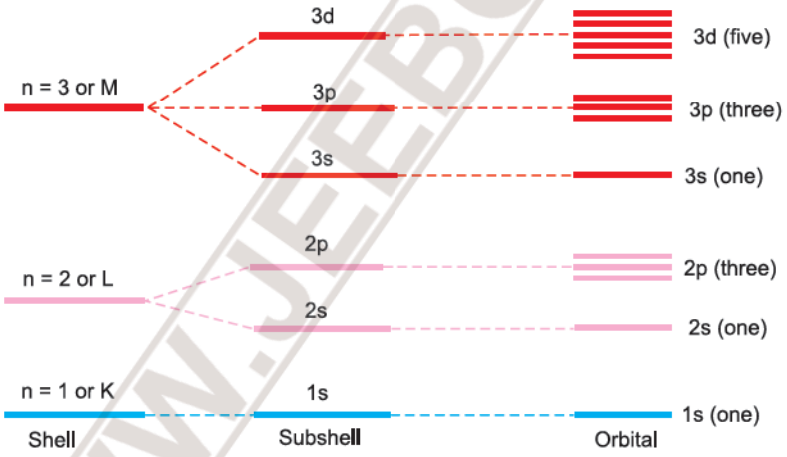

Fig. 31. Number of subshells and orbitals in first three shells (K, L and M).

PAULI'S EXCLUSION PRINCIPLE

After setting the rules for the possible values of quantum numbers, we can calculate the maximum number of electrons that can be added in each shell and subshell in an atom. For this, there is a guiding principle, known as **Pauli's exclusion principle.** It states that

no two electrons in an atom can have same values for all the four quantum numbers.

This principle can be easily understood. We have learnt that an orbital is specified by three quantum numbers n, l and m. Since an electron in an orbital must have the same values of n, l and m, it follows that it can have two values *of* s as either $+\frac{1}{2}$ or $-\frac{1}{2}$. In other words, an orbital can have at the most two electrons provided their spin quantum numbers are different. For example, consider K shell where $n = 1$. It will have one value of l (as $l = 0$) and one value of m (as $m = 0$) but it can have either of the two values of s as $+\frac{1}{2}$ or $-\frac{1}{2}$ *i.e.*,

$n = 1 \quad l = 0 \quad m = 0 \quad s = +\frac{1}{2}$

$n = 1 \quad l = 0 \quad m = 0 \quad s = -\frac{1}{2}$

This leads to the conclusion that an orbital can have maximum of two electrons. Moreover, if an orbital has two electrons, these must be of opposite spins. Thus, **Pauli's exclusion principle** also states that *an orbital can contain maximum of two electrons.*

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From the above discussion, it can be concluded that

***s*-subshell** (containing only **one orbital**) can have a maximum of **2 electrons**

***p*-subshell** (containing **three orbitals**) can have maximum of **6 electrons**

***d*-subshell** (containing **five orbitals**) can have maximum of **10 electrons**

***f*-subshell** (containing **seven orbitals**) can have maximum of **14 electrons**

Thus, it may be concluded that
No. of subshells in nth shell = n
No. of orbitals in a subshell = $(2l + 1)$
No. of electrons in a subshell = $2(2l + 1) = 4l + 2$

It may be noted that the number of electrons in a subshell do not depend upon the value of principal quantum number. From this we can calculate the number of electrons in various shells as given below :

(n = 1) K-shell	**(l = 0) 1s-subshell**	**(m = 0) one orbital**	**2 electrons**
(n = 2) **L-shell**	(l = 0) 2*s*-subshell	(m = 0) *one orbital*	2 electrons
	(l = 1) 2*p*-subshell	(m = – 1, 0, +1) *three orbitals*	6 electrons
		4 orbitals	**8 electrons**
(n = 3) **M-shell**	(l = 0) 3*s*-subshell	(m = 0) *one orbital*	2 electrons
	(l = 1) 3*p*-subshell	(m = –1, 0, +1) *three orbitals*	6 electrons
	(l = 2) 3*d*-subshell	(m = –2, –1, 0, +1, +2) *five orbitals*	10 electrons
		9 orbitals	**18 electrons**
(n = 4) **N-shell**	(l = 0) 4*s*-subshell	(m = 0) *one orbital*	2 electrons
	(l = 1) 4*p*-subshell	(m = –1, 0, +1) *three orbitals*	6 electrons
	(l = 2) 4*d*-subshell	(m = –2, –1, 0, +1, +2) *five orbitals*	10 electrons
	(l = 3) 4*f*-subshell	(m = –3, –2, –1, 0, +1, +2, +3) *seven orbitals*	14 electrons
		16 orbitals	**32 electrons**

Therefore, it may be concluded that the maximum number of orbitals in each shell is $\mathbf{n^2}$ *and maximum number of electrons is* $\mathbf{2n^2}$ *as shown below :*

Shell symbol	K	L	M	N
Shell number (n)	1	2	3	4
No. of orbitals (n^2)	1	4	9	16
No. of electrons ($2n^2$)	2	8	18	32

SOLVED EXAMPLES

❑ **Example 47.**

(a) If the quantum number 'l' has value of 2, what are the permitted values of the quantum number m_l ?

(b) An atomic orbital has n = 3, what are the possible values of l ?

(c) An atomic orbital has l = 3, what are the possible values of m_l ?

Solution : (*a*) If l = 2, the permitted values of m are :

$m_l = -2, -1, 0, +1, +2$

(*b*) For n = 3, l may have the value l = 0, 1, 2

(*c*) For l = 3, m_l may have the values $m_l = -3, -2, -1, 0, +1, +2, +3$.

❑ **Example 48.**

List all the values of l and m for n = 2.

Solution : When n = 2, l can have values 0 and 1

For l = 0, m_l = 0

For l = 1, m_l = – 1, 0, + 1.

❑ **Example 49.**

Using the s, p, d notations, describe the orbital with the following quantum numbers:

(*a*) n = 1, l = 0 (*b*) n = 3, l = 2

(*c*) n = 3, l = 1 (*d*) n = 2, l = 1

(*e*) n = 4, l = 3 (*f*) n = 4, l = 2

N.C.E.R.T.

Solution :

(*a*) $n = 1, l = 0$: 1*s*-orbital

(*b*) $n = 3, l = 2$: 3*d*-orbital

(*c*) $n = 3, l = 1$: 3*p*-orbital

(*d*) $n = 2, l = 1$: 2*p*-orbital

(*e*) $n = 4, l = 3$: 4*f*-orbital

(*f*) $n = 4, l = 2$: 4*d*-orbital

❑ **Example 50.**

(a) What subshells are possible in n = 3 energy level ?

(b) How many orbitals (of all kinds) are possible in this level ?

N.C.E.R.T.

Solution : (*a*) Subshells in n = 3 energy level

We know that the subshells are given by different values of l.

For n = 3, the possible values of l are 0, 1 and 2.

The corresponding subshells are :

l = 0, *s*-subshell; l = 1, *p*-subshell; l = 2, *d*-subshell.

(*b*) Number of orbitals

For n = 3, there are one *s*, three *p* and five *d*-orbitals.

This makes total of nine orbitals in n = 3 level.

❑ **Example 51.**

Explain giving reasons, which of the following sets of quantum numbers are not possible

(*a*) $n = 0, \quad l = 0, \quad m_l = 0, \quad m_s = +\,^1/_2$

(*b*) $n = 1, \quad l = 0, \quad m_l = 0, \quad m_s = -\,^1/_2$

(*c*) $n = 1, \quad l = 1, \quad m_l = -0, \quad m_s = +\,^1/_2$

(*d*) $n = 2, \quad l = 1, \quad m_l = 0, \quad m_s = -\,^1/_2$

(*e*) $n = 3, \quad l = 3, \quad m_l = -3, \quad m_s = +\,^1/_2$

(*f*) $n = 3, \quad l = 2, \quad m_l = 0, \quad m_s = +\,^1/_2$

N.C.E.R.T.

Solution : (*a*) Not possible because n cannot have zero value.

(*b*) Possible

(*c*) Not possible because for n = 1, l = 1 is not possible. l can have values 0, 1 ... (n – 1) only.

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(*d*) Possible
(*e*) Not possible because for $n = 3$, l cannot have 3 value.
(*f*) Possible

Practice Problems

50. Give all possible values of l, m_l and m_s for electrons when $n = 3$.

51. How many electrons in a given atom can have the following quantum numbers ?
(*a*) $n = 3, l = 1$ (*b*) $n = 3, l = 2, m_l = 0$ (*c*) $n = 3, l = 2, m_l = +2, m_s = +\frac{1}{2}$ (*d*) $n = 3$.

52. If the quantum number '*n*' has a value of 3, what are the permitted values of the quantum number '*l* ' ?

53. (*i*) An atomic orbital has n = 3, What are the possible values of l and m_l?
(*ii*) List the quantum numbers (m_l and l) of electrons for 3*d*-orbital.
(*iii*) Which of the following orbital are possible ?
1*p*, 2*s*, 2*p* and 3*f*.

Answers to Practice Problems

50. $l = 0$, $m_l = 0$; $l = 1$, $m_l = -1, 0, +1$; $l = 2$, $m_l = -2, -1, 0, +1, +2$ and $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$ for each value of m_l.

51. (*a*) 6 (*b*) 2 (*c*) 1 (*d*) 18

52. 0, 1, 2.

53. (*i*) $l = 0$, $m_l = 0$; $l = 1$, $m = -1, 0, +1$; $l = 2$, $m_l = -2 - 1, 0, +1, +2$ (*ii*) $l = 2, m_l = -2, -1, 0 + 1, + 2$, (*iii*) 2*s*, 2*p*

Hints & Solutions on page 68

SHAPES OF ATOMIC ORBITALS OR BOUNDARY SURFACE DIAGRAMS

It has been learnt that the probability of finding the electron does not become zero even at large distances from the nucleus. Therefore, it is not possible to draw any sort of geometrical figure that will enclose a region of 100% probability. However, for the sake of pictorial clarity, we draw figures in which the probability of finding the electron is maximum (about 90—95%). These most probable regions *are called boundary surface diagrams* or **orbitals.**

A. Radial Wave Functions

The shapes of orbitals are obtained from the variation of wave function Ψ as a function of *r* (distance from the nucleus). This is also called radial dependence or **radial wave function.** This can be shown in a simple method by plotting a graph between wave function (ψ) and distance (*r*) from the nucleus.

These graphs are shown for 1*s*, 2*s* and 2*p* orbitals in Fig. 32. It is clear from Fig. 32 (*a*) that wave function for 1*s*-orbital continuously decreases with increase in *r*. However, for 2*s*-orbital [Fig. 32 (*b*)] , the wave function decreases in the beginning with increase in *r*, becomes zero at a particular distance and then becomes negative. The wave function for 2*p*-orbital [Fig. 32(*c*)] rises to maximum and then decreases. It is very interesting to note that the 2*s*-wave function can be positive or negative depending upon the distance.

NOTE

It may be noted that the positive and negative signs refer to the sign of the wave function and have no connection to the positive and negative charges.

As we here seen for 2*s* orbtial, at a point, the wave function also becomes zero. This point at which radial wave function becomes zero is called **radial nodal surface or simply node.** At the node, the value of wave function changes from positive to negative. In general, it has been found that *ns* orbitals have $(n - 1)$ nodes. Similarly, *np* orbitals have $(n - 2)$ nodes and so on. For example, the radial wave function for 2*p*-orbital has no node as shown in Fig. 32.

In all cases, Ψ approaches zero as *r* approaches infinity.

It may be noted that like Ψ, the plots of Ψ also do not have physical meaning. However, the importance of these plots lies in the fact that they give information about how the radial wave function changes with distance *r* and about the presence of nodes where the sign of Ψ changes. These have particular importance in understanding the chemical bonding.

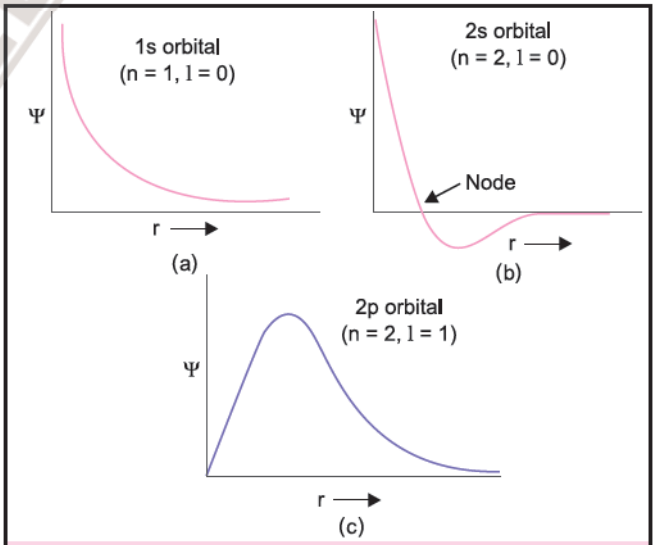

Fig. 32. Plots of wave function (Ψ) with distance from the nucleus for
(*a*) 1*s*-orbital (*b*) 2*s*-orbital (*c*) 2*p*-orbital

B. Probability Density (Ψ^2) Graphs

According to the German physicst, Max Born, the square of the wave function, Ψ^2 at a point gives the probability density of finding the electron at that point.

These variations of Ψ^2 as a function of r are obtained by plotting ψ^2 against *r*.

The plots for 1*s*-, 2*s*- and 2*p* orbitals are shown in Fig. 33 ahead. These diagrams look similar to Fig. 32 except that these become positive throughout (square of negative quantity is always positive). These graphs are called **probability density graphs.**

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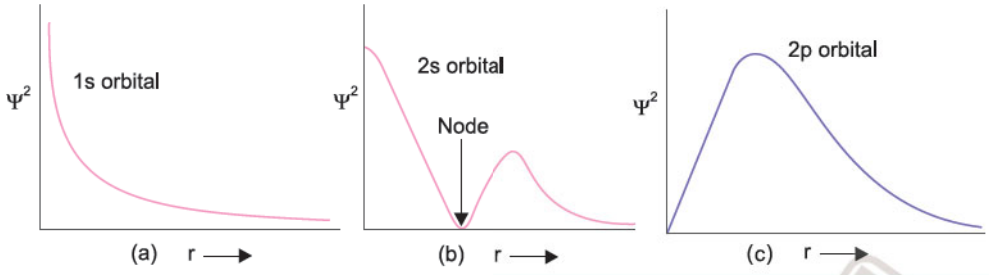


Fig. 33. Variation of ψ^2 with distance from the nucleus for (*a*) 1*s*-orbital (*b*) 2*s*-orbital and (*c*) 2*p*-orbital.

It is clear from Fig. 32 *that for s-orbitals (1s and 2s), the maximum electron density is at the nucleus and for p-orbitals (2p), it has zero electron density at the nucleus.* It may be noted that all orbitals except *s*-orbitals have zero electron density at the nucleus.

Radial Probability Functions ($4\pi r^2\Psi^2$)

The Ψ^2 versus r plots give the probability density for the electron around the nucleus. However, in order to determine the total probability in an infinitesimally small region, we have to multiply probability density (Ψ^2) by the volume of region, *i.e.*

$$\text{Probability} = \Psi^2 \times dV$$

where dV is the volume of the region. Since the atoms have spherical symmetry, it is more useful to discuss the probability of finding the electron in a spherical shell between the spheres of radius $(r + dr)$ and r. To understand this, consider the space around the nucleus to be divided into infinite number of concentric shells. The volume of such a shell of extremely small thickness, dr, is $4\pi r^2\, dr$* so that

$$\text{Probability} = \Psi^2 \times 4\pi r^2\, dr = 4\pi r^2\, dr\, \Psi^2$$

This gives the total probability of finding the electron at a particular distance (r). This is called **radial probability.** The plots of probability ($4\pi r^2\ \Psi^2$) as a function of distance from the nucleus (r) are called **radial probability distribution function** (*r.d.f.*) graphs.

It is clear that the radial probability distribution graphs depend not only upon the probability density but also on the volume of the shell. The probability density (Ψ^2) for 1*s* is maximum near the nucleus and it goes on decreasing with distance (Fig. 33). However, the volume of the shell goes on increasing with increase in distance as shown in Fig. 34 (*a*). The product of probability density and volume of shell gives the radial probability ($4\pi r^2\Psi^2$) and is plotted against the distance from the nucleus [Fig. 34 (*b*)].

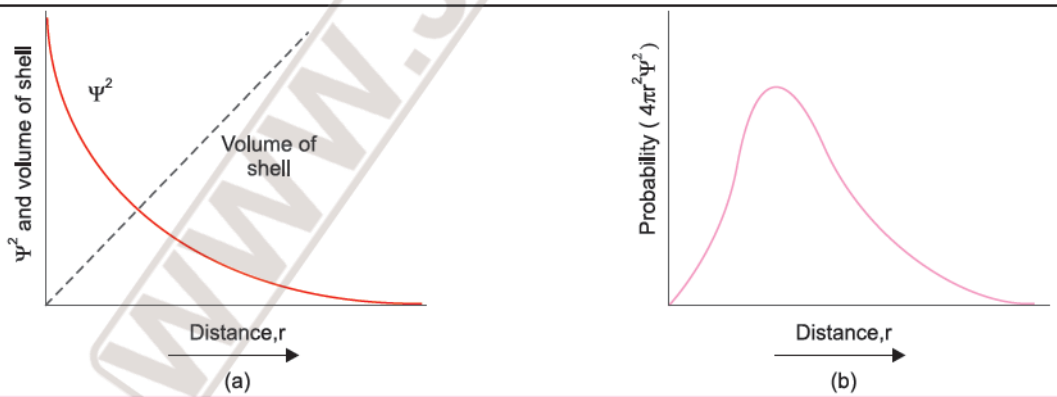
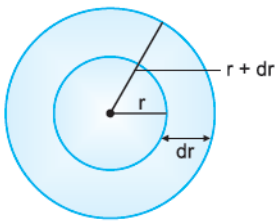


Fig. 34. Radial probability distribution function curve for 1*s*-orbital.

* The volume of the shell is $4\pi r^2 dr$ and it should not be confused with the volume of sphere which is $\frac{4}{3}\pi r^3$. It can be calculated as :



$$\text{Volume of shell} = \begin{bmatrix}\text{Volume of sphere}\\ \text{with radius } (r+dr)\end{bmatrix} - \begin{bmatrix}\text{Volume of sphere}\\ \text{with radius } r\end{bmatrix} = \frac{4}{3}\pi(r+dr)^3 - \frac{4}{3}\pi r^3$$

$$= \frac{4}{3}\pi[r^3 + 3r^2dr + 3rdr^2 + dr^3] - \frac{4}{3}\pi r^3 = \frac{4}{3}\pi[r^3 + 3r^2dr] - \frac{4}{3}\pi r^3$$

(As dr represents an extremely small thickness, the higher powers of dr such as dr^2 and dr^3 may be neglected)

$$\text{Volume of shell} = \frac{4}{3}\pi \times 3r^2dr = 4\pi r^2dr$$

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The graph for 1*s*-orbital shows that the probability of finding the electron is zero at nucleus, it keeps on increasing and becomes maximum at a particular distance from the nucleus and then gradually decreases. The peak of the curve gives the distance from the nucleus where the probability of finding the electron is maximum. This is called the **radius of maximum probability.** For hydrogen atom, this distance has been found to 52.9 pm (or 0.529 Å). This value agrees well with the value calculated by Bohr for the radius of first orbit.

It is important to note that Bohr predicted that the electron will always be at r = 52.9 pm for H atom. However, according to wave mechanics, the electron is most likely to be found at this distance but there is probability of finding the electron at distances shorter and larger than 52.9 pm.

The radial probability distribution function for 2*s* orbital is shown in Fig. 35(*b*). The curve shows that there are two regions of high probability (maxima). In between the regions of maximum probabilities, there is a region where the probability of finding the electron is zero. It is called **node.** The radial probability function for 2*p* orbital is also shown in Fig. 35(*c*).

The radial probability functions versus distance *r* from the nucleus for 1*s*, 2*s* and 2*p* orbitals are shown in Fig. 35.

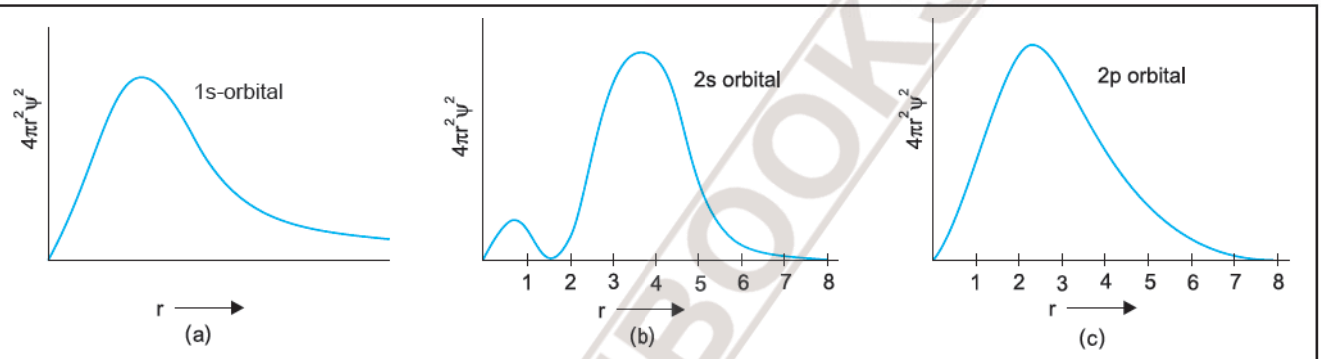

Fig. 35. Radial probability functions as a function of distance, *r* from the nucleus for (*a*) 1*s* (*b*) 2*s* and (*c*) 2*p* orbital.

NOTE

It may be noted that the distance of maximum probability for a 2*p* orbital is slightly less than that for a 2*s* electron. However, in contrast to a 2*p*-curve, there is a small additional maxima in the 2*s* curve. This indicates that the electron in 2*s* orbital spends some of its time near the nucleus. In other words, the 2*s* electron penetrates a little closer to the nucleus than the 2*p*-electron. As a result, 2*s* electron is attracted more strongly by the nucleus than a 2*p*-electron. That is why, 2*s* electron is more stable and, hence, has lower energy than a 2*p*-electron.

Boundary Surface Diagrams

The shapes of orbitals may be represented in terms of boundary surfaces diagrams. In this representation, a boundary surface is drawn for an orbital representation which encloses maximum probability (about 90%) of finding the electron. In other words, boundary surface diagrams give the **most probable regions.**

These boundary surface diagrams of some orbitals are discussed below :

1. Shapes of *s*-orbitals

s-orbitals are non-directional and spherically symmetrical. This means that the probability of finding the electron is same in all directions at a particular distance from the nucleus. The 1*s*-orbital is shown in Fig. 36 ahead. It is observed that density of charge cloud is maximum at the nucleus and decreases with increase in distance from the nucleus.

The 2*s*-orbital is also non-directional and spherically symmetrical. In this case, the probability density is maximum at the nucleus and becomes small at large distances. However, the effective volume or size of 2*s* is larger than 1*s*-orbital. An important feature of 2*s*-orbital is that there is a spherical shell within 2*s*-orbital (region without dots) where the probability of finding the electron is practically zero. This is called a **node** or a **nodal surface**. Thus, *a 2s-orbital differs from 1s-orbital in being larger in size and having a nodal surface.*

For the sake of simplicity, the boundary surface diagram for 1*s* orbital is shown in Fig 36 (*c*) instead of giving its charge cloud.

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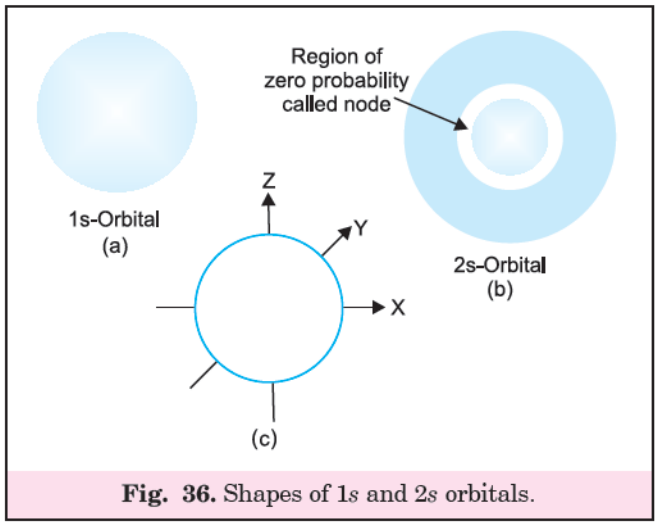

Fig. 36. Shapes of 1*s* and 2*s* orbitals.

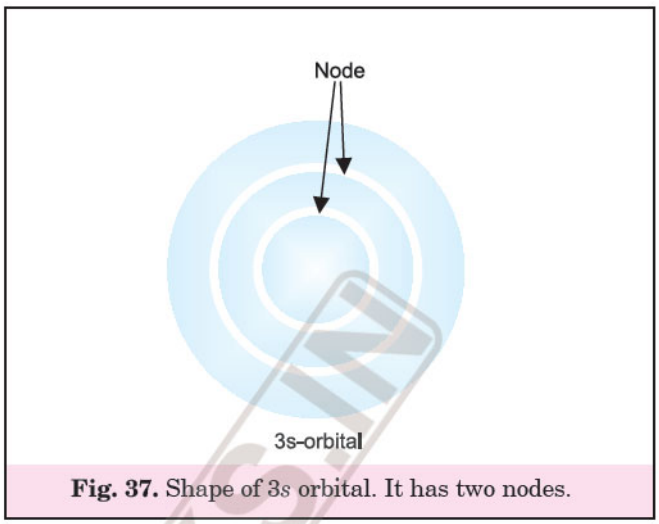

Fig. 37. Shape of 3*s* orbital. It has two nodes.

The higher *s*-orbitals have also spherical shapes and number of nodal surfaces in *s*-orbital for any given energy level is $n - 1$, where n represents energy level. For example, the shape of 3*s* orbital is shown in Fig. 37. It has two nodes.

It is also observed that the size of s-orbital increases with increase in value of n *i.e.*, $4s > 3s > 2s > 1s$ and the electron is located further away from the nucleus as the principal quantum number increases.

2. Shapes of *p*-orbitals

For *p*-orbitals ($l = 1$), there are three possible orientations corresponding to $m_l = -1, 0, +1$ values. This means that there are three *p*-orbitals in each *p*-subshell. These are designated as p_x, p_y and p_z; for example, $2p_x$, $2p_y$ and $2p_z$. These three orbitals are equal in energy but differ in their orientations. Each orbital consists of two lobes symmetrical about a particular axis. Depending upon the orientation of the lobes, these are designated as $2p_x$, $2p_y$ and $2p_z$ according as they are symmetrical about x, y and z-axes respectively. That is, $2p_x$ orbital has two lobes symmetrical around x-axis and $2p_y$ orbital has two lobes symmetrical around y-axis while the lobes of $2p_z$ orbital are symmetrical around z-axis (Fig. 38). The shape of the orbital is called **dumb bell** shape. For the sake of simplicity a $2p$ orbital (e.g., $2p_x$) is shown by simple boundary surface as given in Fig. 38 (*d*).

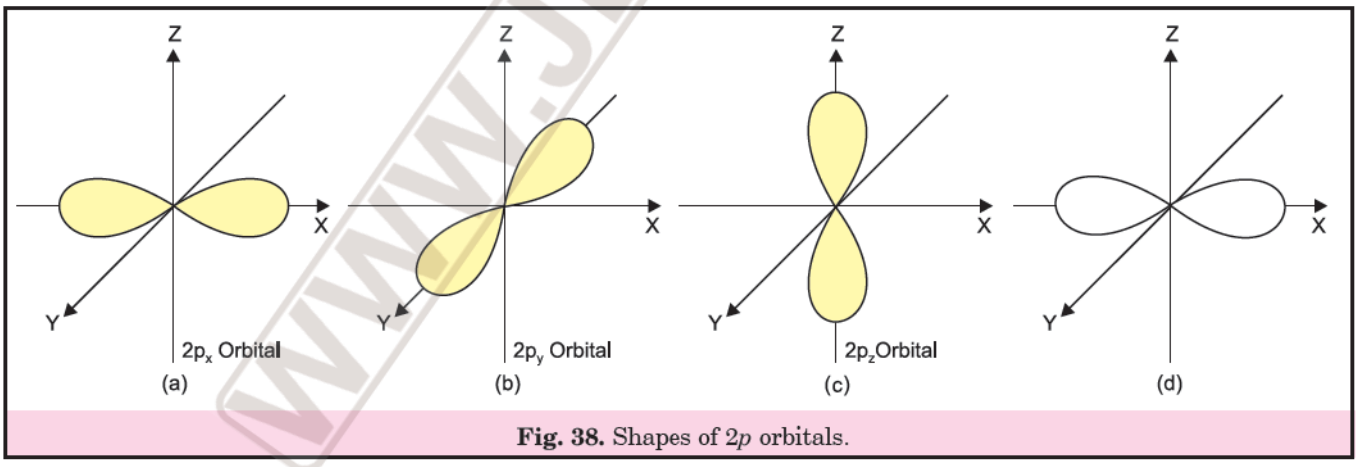

Fig. 38. Shapes of 2*p* orbitals.

It may be noted that the two lobes of a *p*-orbital are separated by a plane having zero electron density. This is called **nodal plane.** The nodal planes for $2p_x$, $2p_y$ and $2p_z$ orbitals are shown in Fig. 39 ahead.

It should be noted that the probability of finding the electron in a particular *p*-orbital is equal in both lobes. The *p*-orbitals of higher energy levels ($n = 3, 4, 5$....etc.) have similar shapes although their sizes are bigger. The size of *p*-orbital increases with increase in value of n as $4p > 3p > 2p$.

Like *s*-orbitals, *p*-orbital also passes through zero probability region and number of nodes is *p*-orbitals are given by $n - 2$ *i.e,* for 3*p*-orbital number of radial nodes is one, two for 4*p* orbital and so on.

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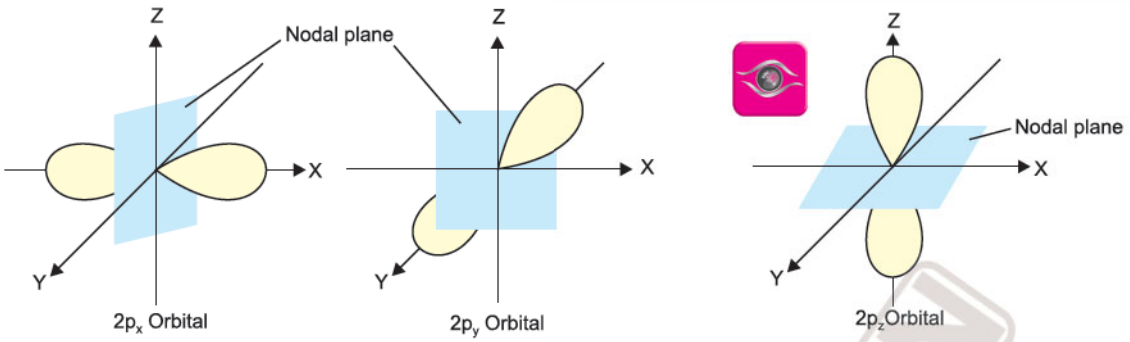

Fig. 39. Nodal planes in 2*p* orbitals.

3. Shapes of *d*-orbitals

For *d*-orbital (l = 2), there are five possible orientations corresponding to m_l = – 2, – 1, 0, + 1, + 2. This means that there are **five orbitals** in each *d*-subshell. For 3*d*-subshell, these are designated as $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$ and $3d_z^2$. These five orbitals are equal in energy but differ in their orientations. The shapes of these orbitals are described below :

(*i*) The three orbitals d_{xy}, d_{yz} and d_{zx} are similar and each consists of four lobes of high electron density lying in *xy*, *yz* and *zx* planes respectively. These lobes lie in between the principal axes. For example, in case of d_{xy} orbital, the four lobes lie in *xy* plane in between the *x* and *y*-axes.

(*ii*) The $d_{x^2-y^2}$ orbital has also four of high electron density along the principal axes *x* and *y*. *It may be noted that this orbital is exactly like dxy orbital except that it is rotated through 45° around the z-axis.*

(*iii*) The d_{z^2} orbital consists of two lobes along the *z*-axis with a ring of high electron density in the *xy* plane. The shapes of 3*d*-orbitals are shown in Fig. 40.

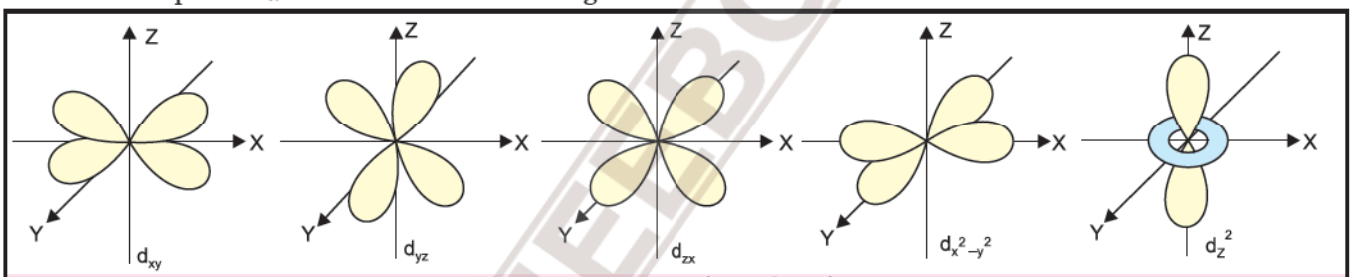

Fig. 40. Shapes of five 3*d*-orbitals.

Nodes and Nodal Planes

A spherial surface within an orbital on which the probability of finding the electron is zero is called **spherical node** or **radial node**. These correspond to positions at which radial wave function passes through zero.

The number of spherical or radial nodes in an orbital = **$(n - l - 1)$**

For example, 1*s* orbital (n = 1, l = 0) has no node, 2*s* orbital; (n = 2, l = 0) has **one** node, 2*p* orbital (n = 2, l = 1) has **no** node, 3*p* orbital (n = 3, l = 1) has **one** node and so on....

Beside radial nodes, the probability density functions for *np* and *nd* orbitals are zero at the planes passing through the nucleus. *A plane passing through the nucleus on which the probability of finding the electron is zero* is called a **nodal plane**. For example as shown in Fig. 39, in case of $2p_x$ orbital, *yz* plane is a nodal plane. This is also called **angular node.** Similarly, four 3*d* orbitals ($3d_{xy}$, $3d_{yz}$, $3d_{zx}$ and $3d_{x^2-y^2}$) have two perpendicular nodal planes that intersect in a line passing through the nucleus. For example, $3d_{xy}$ orbital has two nodal planes, passing through the origin and bisecting the *xy* plane containing *z*-axis. The number of **angular nodes or nodal planes are given by 'l'** *i.e*, one angular node for *p* orbitals (l = 1); two angular nodes for *d*-orbitals (l = 2) and so on.

In general, in an orbital :

Total number of nodes = $n - 1$

Angular nodes = l

Radial nodes = $n - l - 1$.

For example,

Radial nodes

Orbital	No. of nodes	Orbital	No. of nodes
1 *s*	0	3 *d*	0
2 *s*	1	4 *d*	1
3 *s*	2	5 *d*	2
2 *p*	0	4 *f*	0
3 *p*	1	5 *f*	1
4 *p*	2	6 *f*	2

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Angular nodes

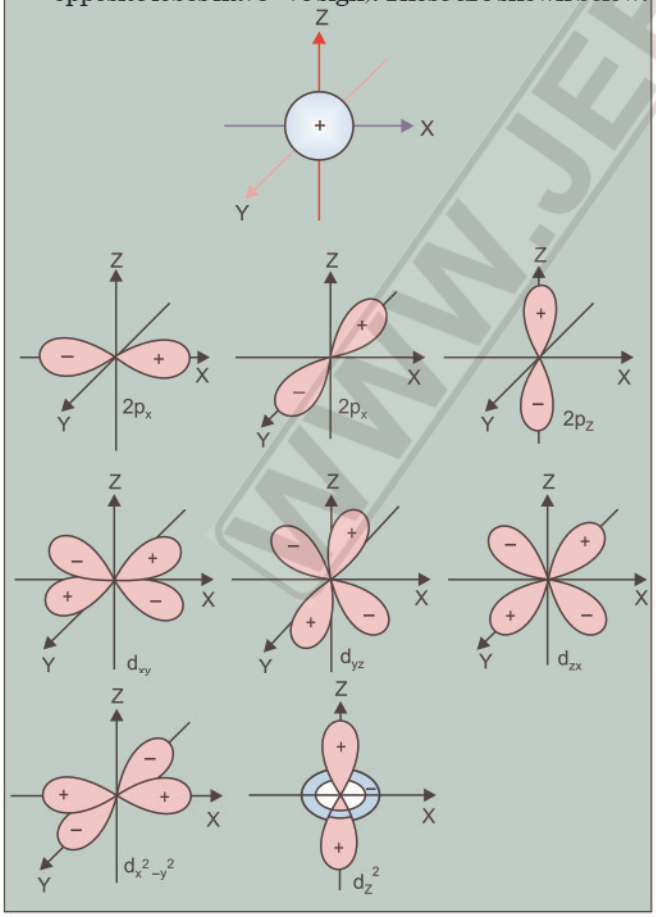
Orbital	No. of angular nodes
s	0
p	1 plane for each orbital
d	2 planes for each orbital*

*It may be noted that d_{z^2} orbital has one conical surface which is counted as two angular nodes.

NOTE

It may be noted that the shapes of orbitals represent plots of probability density (ψ^2) and are therefore, always positive. But sometimes sketches of wave function (ψ) are also plotted. These have +ve and –ve lobes. **The signs in the lobes represent the sign of the wave function in different directions.** The wave functions may have +ve or –ve signs. These graphs of wave functions are very important in understanding the bonding between atoms (discussed in unit 4). These +ve and –ve signs have nothing to do with positive or negative charge. It may be remembered that

- s-orbitals are always positive.
- The opposite lobes of p-orbitals have **opposite signs** (one +ve, the other –ve).
- The opposite lobes of d-orbitals have **same sign** (two opposite lobes have +ve sign while the other two opposite lobes have –ve sign). These are shown below:



ENERGY LEVEL DIAGRAM FOR ELECTRONS IN AN ATOM

The relative energies of various orbitals can be shown by an arrangement known as **energy level diagram.** The energy level diagram for hydrogen atom is given in Fig. 41. It is clear from the figure that *the energies of various orbitals in a hydrogen atom depend only upon the value of principal quantum number (n) and independent of the value of l.* In other words, all the subshells in a given principal shell *i.e., s, p, d* and *f* have same energies. For example, 2*s*- and 2*p*-orbitals have same energies. Similarly, all the orbitals of third shell (n = 3) *i.e.,* 3*s*, 3*p* and 3*d* have same energies and all the orbitals of fourth shell (n = 4), *i.e.,* 4*s*, 4*p*, 4*d* and 4*f* have same energies.

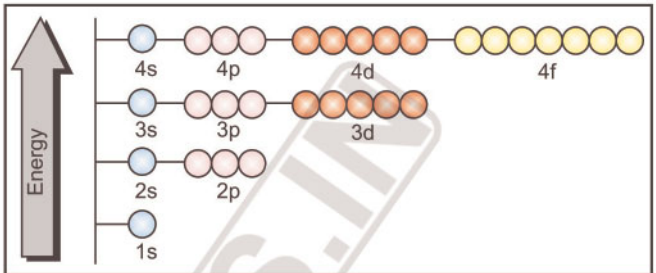


Fig. 41. Energies of different orbitals in a hydrogen atom

$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$

The orbitals having the same energy are called ***degenerate orbitals.*** The electron in 1s orbital in hydrogen atom corresponds to most stable state and is called **ground state.** An electron in the 2*s*, 2*p* or higher orbital in a hydrogen atom is called **excited state.**

However, in the case of **multielectron atom,** the energies of orbitals having the same value of n but different values of l are different. This means that energies of the orbitals depend upon the value of n as well as l. In other words, the different subshells of the same energy shell have different values. For example, 2*s* and 2*p*-orbitals have different energies. The three subshells of n = 3 *i.e.,* 3*s*, 3*p* and 3*d* have different energies. Similarly, the subshells for n = 4, *i.e.* 4*s*, 4*p*,

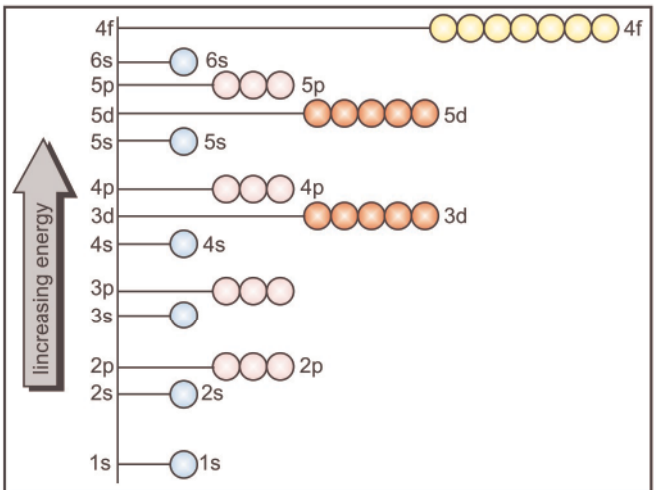


Fig. 42. Energies of different subshells and orbitals in a multielectron atom.

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4*d* and 4*f*-subshell have different energies as shown in Fig. 42. The main reason for having different energies of the subshells is the mutual repulsion among electrons in a multielectron atom. In case of hydrogen atom, the only interaction present is the attraction between the negatively charged electron and the positively charged nucleus. However, in multielectron atoms, besides the presence of attraction between the electron and the nucleus, there are repulsion terms between every electron and other electrons present in the atom.

Cause of different energy patterns of hydrogen atom and multielectron atoms : The energy on an electron in an orbital depends upon the following factors :

(*i*) *nuclear charge*
(*ii*) *principle energy level,*
(*iii*) *the presence of electrons in the lower energy levels.*

In a multielectron atom, the electrons occupying the inner energy levels tend to reduce the effect of nuclear charge on the electrons present in the outermost energy level. In other words, the electrons in the inner shells screen or shield the outermost electrons form the nucleus. This effect is known as **screening** or **shielding effect.** This is different in different types of orbitals. The net positive charge experienced by the electron from the nuclear is called effective nuclear charge (Z_{eff}).

For example, being spherical in shape, s-orbital electron, spends more time closer to the nucleus in comparison to *p*-orbitals and *p*-orbital spends more time near the nucleus in comparison to *d*-orbital. In orther words, *s*-orbital will be screened lass then a *d*-orbital for given shell. In other wards effective nuclear charge (Z_{eff}) experienced by the orbital decreases with increase of azimuthal quantum number (l). This means the *s*-orbitals will be more tightly bound to the nucleus than *p*-orbitals while *p*-orbitals will be more tightly bound to the nucleus than *d*-orbitals and so on. Thus, the energy of different orbitals will increase as

$$s < p < d \ .....$$

However, in the case of hydrogen atom, there is only one electron and therefore, no shielding effect. As a result, the different orbitals (*s*, *p*, *d* and *f*) of the same energy level have same energies.

From Fig. 40, the following points are clear :

(*i*) *For the same value of n, the higher the value of l, the higher is the energy.* Thus, 2*p*-orbital ($n = 2$, $l = 1$) has more energy than 2*s*-orbital ($n = 2$, $l = 0$). Similarly, the energies of subshells for $n = 3$ are in the order:
$3s$ ($n = 3$, $l = 0$) < $3p$ ($n = 3$, $l = 1$) < $3d$ ($n = 3$, $l = 2$)

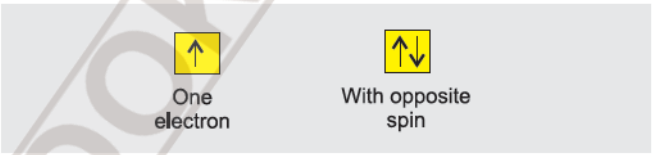
(*ii*) *The difference of energies of s and p-orbitals is small for the same value of n but the difference of p- and d-orbitals is large and so on.*

(*iii*) *In some cases, the sub-level of higher energy shell falls below the sub-level of a lower energy shell.* For example, the energy of 4*s*-orbital is less than that of a 3*d*-orbital. Similarly, 5*s*-orbital is lower in energy than 4*d*-orbital.

(*iv*) The energy of various orbitals increases in the order :
1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*.

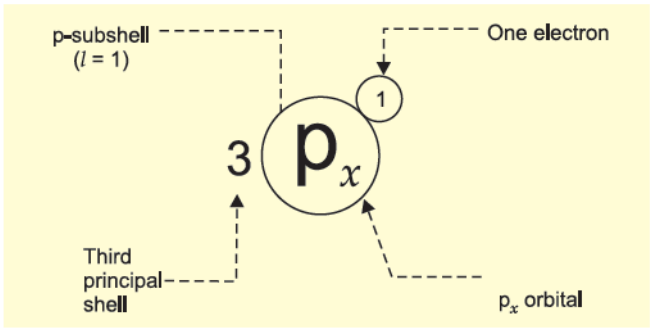
ELECTRONIC CONFIGURATIONS OF ATOMS

The filling of orbitals in an atom is a hypothetical process in which the atom is built up by feeding electrons in orbitals, one at a time and by placing each new electron in the lowest available energy orbital. *The distribution of electrons in different orbitals is known as* **electronic configuration of the atom.** This characterises each electron in an atom. For the sake of presentation, the following symbols are commonly used :



A box for an orbital (square or circular); an arrow for an electron, the direction of the arrow giving the orientation of its spin. Two arrows are shown for two electrons with opposite orientations of spin.

Alternatively, electronic configuration is expressed by indicating the principal quantum number and its respective orbital along with the number of electrons present in it. For example, the notation $3p_x^1$ indicates that there is one electron in p_x orbital of third principal shell.



The filling of orbitals is governed by the following principles :

1. Aufbau principle. The Aufbau principle states that

in the ground state of the atoms, the orbitals are filled in order of their increasing energies. In other words, electrons first occupy the lowest-energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled.

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The word *aufbau* in German means *building up*. The building up of the orbitals means the filling up of orbitals with electrons. From an energy level diagram (Fig. 42) for multi-electron atoms, the following sequence is observed for orbitals in the increasing order of energy:

1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*

According to Aufbau principle, the orbital should be filled in the above sequence.

It is very important to remember that the sequence of energy levels pertains up to 3*p* and then 4*s*-orbital comes first instead of 3*d*. In fact, the energy of an orbital is determined by the quantum numbers n and l with the help of important rule known as $(n + l)$ rule or **Bohr Bury's rule.** According to this :

(i) *Orbitals fill in the order of increasing value of $n + l$. For example, 3s-orbital $(n + l = 3 + 0 = 3)$ will be filled before 4s $(n + l = 4 + 0 = 4)$ orbital. Similarly, out of 3d and 4s, the 4s $(n + l = 4 + 0 = 4)$ orbital will be filled before 3d $(n + l = 3 + 2 = 5)$ orbital.*

(ii) *If the two orbitals have same value of $(n + l)$, then the orbital with lower value of n will be filled first.* For example, 2*p*-orbital $(n + l = 2 + 1 = 3)$ and 3*s*-orbital $(n + l = 3 + 0 = 3)$ have the same $(n + l)$ value but 2*p*-orbital has lower value of n and therefore, it will be filled first. This is shown below in Table 5.

Table 5. Arrangement of orbitals with increasing energy on the basis of $(n + l)$ rule

Orbital	Value of n	Value of l	Value of $(n + l)$	
1 *s*	1	0	1 + 0 = 1	
2 *s*	2	0	2 + 0 = 2	
2 *p*	2	1	2 + 1 = 3	2*p* (n = 2) has lower energy than 3s (n = 3)
3 *s*	3	0	3 + 0 = 3	
3 *p*	3	1	3 + 1 = 4	3*p* (n = 3) has lower energy than 4*s* (n = 4)
4 *s*	4	0	4 + 0 = 4	
3 *d*	3	2	3 + 2 = 5	3*d* (n = 3) has lower energy than 4*p* (n = 4)
4 *p*	4	1	4 + 1 = 5	

This rule also helps to account for the fact that certain orbitals with higher value of n but lower value of l have less energy than orbitals with lower value of n and higher value of l. For example, let us apply this rule to 4*s*- and 3*d*-orbitals. For 3*d*-orbital $(n + l)$ value = 3 + 2 = 5 while for 4*s*-orbital $(n + l)$ value = 4 + 0 = 4. Thus, 4*s*-orbital has lesser energy than 3*d*-orbital and, therefore, is filled first.

The sequence of energy levels can be easily remembered by the systematic diagram as shown in Fig. 43. Starting from the top, the direction of the arrows gives the order of filling of orbitals in starting from right top to bottom left.

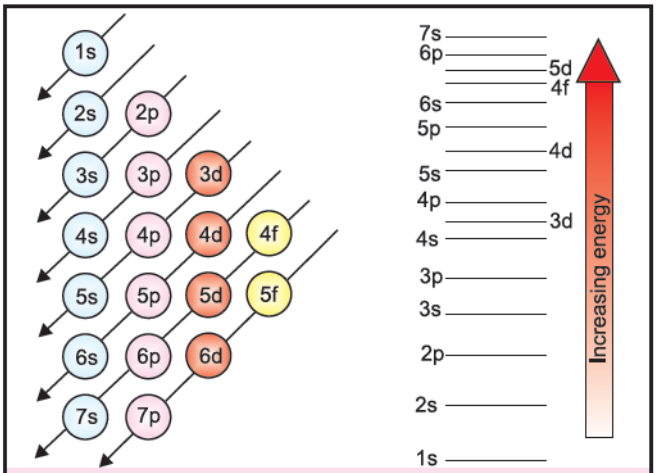

Fig. 43. Schematic diagram to remember sequence of filling atomic orbitals.

2. Pauli's exclusion principle. According to this principle, an ***orbital can accommodate maximum of two electrons and these must have opposite spins.***

This principle thus limits the accommodation of electrons in an orbital. This means that an orbital can have 0, 1 or 2 electrons. Moreover, if an orbital has two electrons, they must be of opposite spins.

3. Hund's rule of maximum multiplicity. According to this rule,

electron pairing will not take place in orbitals of same energy (same subshell) until each orbital is singly filled.

This suggests that it is difficult for an electron to enter an orbital which already has an electron than to enter an unoccupied orbital of same energy. This principle is very important in guiding the filling of *p*, *d*

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and *f* orbitals, which have more than one kind of orbitals. For example, we know that there are three *p*-orbitals (p_x, p_y and p_z) of the *p*-subshell in a principal energy level. According to Hund's rule, each of the three *p*-orbitals must get one electron of parallel spin before any one of them receives the second electron of opposite spin.

Electronic Configurations of Atoms

Based upon the above rules and the sequence of energy levels, let us write the electronic configurations of some atoms.

Hydrogen (At. No. = 1). Since hydrogen has only one electron, it must go to 1*s*-orbital which has lowest energy.

H : (Z = 1) $1s^1$ or

Helium (At. No. = 2). In helium atom, the second electron can also go into 1*s*-orbital. The two electrons must have opposite spins (Pauli's exclusion principle).

He : (Z = 2) $1s^2$ or

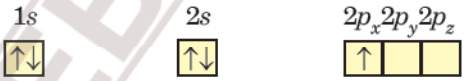
Lithium (At. No. = 3). Since 1*s*-orbital is filled with two electrons, it cannot have any more. Therefore, the third electron goes to the next lowest energy orbital, namely 2*s-orbital*.

Li : (Z = 3) $1s^2 2s^1$ or

Beryllium (At. No. = 4). The fourth electron in beryllium fills 2*s*-orbital.

Be : (Z = 4) $1s^2\ 2s^2$ or

Boron (At. No. = 5). In this case, the fifth electron goes into any one of the 2*p* orbitals (say $2p_x$) :

B : (Z = 5) $1s^2 2s^2 2p_x^1$ or 

It may be remembered here that the fifth electron can enter any of the three $2p_x$, $2p_y$ or $2p_z$ orbitals because all are of the same energy. It is only a matter of convention that we fill the orbitals in the order of $2p_x$, $2p_y$ and $2p_z$.

Carbon (At. No. = 6). In carbon atom, the sixth electron is also to go into the 2*p*-orbitals because it can accommodate six electrons. Here Hund's rule applies, *i.e.,* the electrons enter the orbitals of same energy with parallel spin until all are singly filled. Therefore, the sixth electron cannot enter the $2p_x$ orbital, rather it can go into either $2p_y$ or $2p_z$ in accordance with Hund's rule :

C : (Z = 6) $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$ or

Nitrogen (At. No. = 7). Applying Hund's rule, nitrogen atom has three unpaired electrons in 2*p*-orbitals as :

N : (Z = 7) $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$ or

Oxygen (Z = 8), fluorine (Z = 9) and neon (Z = 10). Beginning with oxygen, the 2*p*-orbitals start getting filled by second electron till each of these is completely filled.

O : (Z = 8) $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$ or

F : (Z = 9) $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$ or

Ne : (Z = 10) $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$ or

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Sodium (Z = 11) to Argon (Z = 18). The electronic configurations of these atoms are written exactly in the same manner as discussed above. Here, 3*s*- and 3*p*-orbitals are filled as did 2*s*- and 2*p*-orbitals in Li to Ne.

Furthermore, for simplicity a common convention is used. In this, the detailed electronic configuration of the noble gas core preceding the valence shell is represented by the symbol of the noble gas in square brackets. Then, the configuration of the valence shell is written after the symbol.

For example, the electronic configuration of sodium may be written as Na (Z = 11) : [Ne]$3s^1$.

The electronic configurations of these elements are given below :

Sodium, Na (Z = 11)	[Ne] $3s^1$
Magnesium, Mg (Z = 12)	[Ne] $3s^2$
Aluminium, Al (Z = 13)	[Ne] $3s^2\ 3p_x^1$
Silicon, Si (Z = 14)	[Ne] $3s^2\ 3p_x^1\ 3p_y^1$
Phosphorus, P (Z = 15)	[Ne] $3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$
Sulphur, S (Z = 16)	[Ne] $3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$
Chlorine, Cl (Z = 17)	[Ne] $3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$
Argon, Ar (Z = 18)	[Ne] $3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$

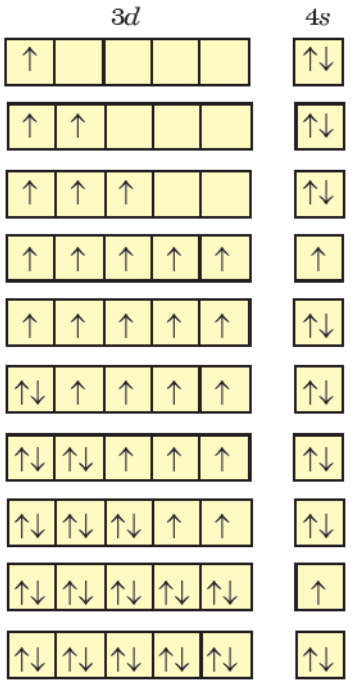
Potassium (Z = 19) and calcium (Z = 20). In these atoms, electrons enter the 4*s*-orbital in accordance with the fact that 4*s*-orbital is slightly lower in energy than 3*d*-orbital.

Potassium, K (Z = 19) : [Ar] $4s^1$

Calcium, Ca (Z = 20) : [Ar] $4s^2$

Scandium (Z = 21) to zinc (Z = 30). With scandium (Z = 21), 3*d*-subshell comes into use and from scandium to zinc, this subshell is gradually filled up. The electronic configurations of the elements from scandium (Z = 21) to zinc (Z = 30) are given below :

Scandium,	Sc (Z = 21)	:	[Ar] $3d^1\ 4s^2$	or	
Titanium,	Ti (Z = 22)	:	[Ar] $3d^2\ 4s^2$	or	
Vanadium,	V (Z = 23)	:	[Ar] $3d^3\ 4s^2$	or	
Chromium,	**Cr (Z = 24)**	**:**	**[Ar] $3d^5\ 4s^1$**	or	
Manganese,	Mn (Z = 25)	:	[Ar] $3d^5\ 4s^2$	or	
Iron,	Fe (Z = 26)	:	[Ar] $3d^6\ 4s^2$	or	
Cobalt,	Co (Z = 27)	:	[Ar] $3d^7\ 4s^2$	or	
Nickel,	Ni (Z = 28)	:	[Ar] $3d^8\ 4s^2$	or	
Copper,	**Cu (Z = 29)**	**:**	**[Ar] $3d^{10}\ 4s^1$**	or	
Zinc,	Zn (Z = 30)	:	[Ar] $3d^{10}\ 4s^2$	or	



Exceptional Configurations of Chromium and Copper

From the above configurations, it may be noted that there are two irregularities in the general trend. The electronic configurations of Cr and Cu are different than what we expected. The electronic configurations for these atoms are expected to be

Cr : [Ar] $3d^4\ 4s^2$ and Cu : [Ar] $3d^9\ 4s^2$

However the **actual configurations** are

Cr : [Ar] $3d^5\ 4s^1$ and Cu : [Ar] $3d^{10}\ 4s^1$

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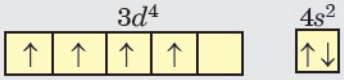
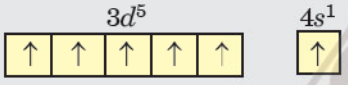
This is attributed to the fact that half-filled (containing one electron per orbital) and completely filled (containing two electrons per orbital) electronic configurations have lower energy and, therefore, extra stability. Consequently, the configurations, d^5, d^{10}, f^7 and f^{14} which are either half-filled or completely-filled, are more stable. Thus, to acquire increased stability, one of the 4*s*-electrons goes into the nearby 3*d*-orbitals so that 3*d*-orbitals get half-filled in Cr and completely-filled in Cu.

The extra stability of half-filled and completely-filled electronic configurations is due to their *(i) symmetrical arrangement and (ii) large exchange energy as explained below :*

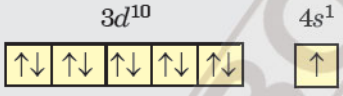
(*i*) **Stability on the basis of symmetrical distribution of electrons.** The symmetry leads to stability. Therefore, the electronic configurations in which all the orbitals of the same subshell are either completely-filled or exactly half-filled are more stable because of symmetrical distribution of electrons. For example, the expected configuration of Cr (Z = 24) is :



But if one electron is shifted from 4*s*- to 3*d*-subshell, the distribution of electrons become more symmetrical and more stable.



Similarly, in case of copper, when an electron is shifted from 4*s*- to 3*d*-subshell, the 3*d*-subshell becomes more stable due to symmetrical arrangement.



(*ii*) **Stability due to exchange energy.** The half-filled and completely-filled electronic configurations are also stable due to large exchange of energy of stabilization.

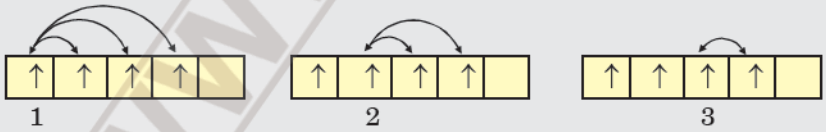
The exchange means the shifting of electrons from one orbital to another in the same subshell. This can be easily illustrated by considering the example of chromium.

If the electronic configuration of Cr is $3d^4\ 4s^2$, then the electron in *d*-subshell can exchange in the following ways :

(*i*) The first electron (number 1) can exchange its positions with electrons numbered 2, 3 and 4 *i.e.,* in *3 ways*.

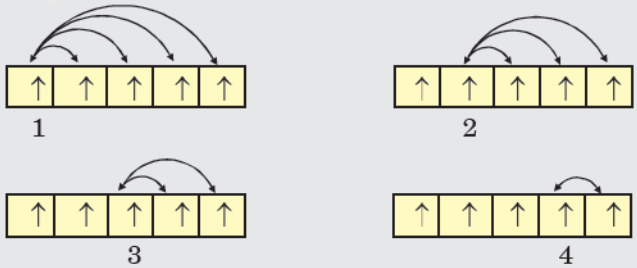
(*ii*) The second electron (number 2) can exchange its positions in *two ways* with electrons 3 and 4 only because the exchange of position between 1 and 2 has already been considered in step (*i*).

(*iii*) The electron (number 3) can exchange only in one way *i.e.* with electron 4.



Thus, in $3d^4$ arrangement, electrons can exchange in 3 + 2 + 1 = 6 ways or there are six possible arrangements with parallel spins in $3d^4$ configuration.

On the other hand, in $3d^5$ configuration, the electron can exchange in *10 ways* as shown below :



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It is clear that the electron 1 can exchange in *four ways*, the electron 2 in *three ways*, electron 3 in *two ways* and electron 4 in *one way*. Thus, total number of ways of exchanging electron in $3d^5$ configuration are 4 + 3 + 2 + 1 = 10. Since the number of exchanges in $3d^5\ 4s^1$ configuration is more than that in $3d^4\ 4s^2$ configuration, therefore, the greater exchange is responsible for the extra stability of this configuration.

Similarly, it can be seen that the exchange energy for d^{10} electronic configuration is more than for d^9 configuration. Thus, the greater exchange for half-filled and completely-filled configurations gives them extra stability.

Gallium (Z = 31) to Krypton (Z = 36). With gallium onwards, 4*p*-orbitals get filled up as :

Gallium	Ga (Z = 31)	:	[Ar] $3d^{10}\ 4s^2\ 4p_x^1$
Germanium	Ge (Z = 32)	:	[Ar] $3d^{10}\ 4s^2\ 4p_x^1\ 4p_y^1$
Arsenic	As (Z = 33)	:	[Ar] $3d^{10}\ 4s^2\ 4p_x^1\ 4p_y^1\ 4p_z^1$
Selenium	Se (Z = 34)	:	[Ar] $3d^{10}\ 4s^2\ 4p_x^2\ 4p_y^1\ 4p_z^1$
Bromine	Br (Z = 35)	:	[Ar] $3d^{10}\ 4s^2\ 4p_x^2\ 4p_y^2\ 4p_z^1$
Krypton	Kr (Z = 36)	:	[Ar] $3d^{10}\ 4s^2\ 4p^6$

Note. *To write the electronic configuration of an atom, it is better if we remember the atomic number of noble gases and the orbitals which follow the noble gas. Then the next orbitals to be filled can be seen from the general sequence. The noble gases with their atomic numbers and orbitals which follow these noble gas cores are given below :*

$[He]^2\ 2s$; $[Ne]^{10}\ 3s$; $[Ar]^{18}\ 4s$; $[Kr]^{36}\ 5s$; $[Xe]^{54}\ 6s$; $[Rn]^{86}\ 7s$.

For example, let us try to write the electronic configuration of I(Z = 53). The noble gas having atomic number less than 53 is $[Kr]^{36}$ and orbital which follows this is 5s. After 5s the orbitals with increasing energies are 4*d*, 5*p* ..... so that

I (Z = 53) : [Kr] $4d^{10}\ 5s^2\ 5p^5$

In the next eighteen elements from rubidium (Rb) to Xenon (Xe), the orbitals which are being gradually filled are 5*s*, 4*d* and 4*p* similar to that of 4*s*, 3*d* and 4*p* orbitals as discussed above. Then 6*s* orbitals are filled for Cs and Ba with one and two electrons respectively. Then from lanthanum (La) to mercury (Hg), the filling up of electrons takes place in 4*f* and 5*d* orbitals. After this, the filling of 6*p*, then 7*d* and finally 5*f* and 6*d* orbitals takes place. However, it may be noted that there are many anomalous configurations due to stability of half filled and completely filled orbitals.

The electronic configurations of all elements are given in Table 6. It may be noted that it is very important to know the elecronic configuration of atoms. The chemical behaviour of an atom depends on the distribution of electrons in various shells, subshells or orbitals. The tendency of atoms to take part in chemical combination also depends on the electrons in the outermost shell (called valence shell). Therefore, a detailed understanding of the electronic structure of atoms is very essential for getting an insight into the various aspects of modern chemical knowledge.

Table 6. Electronic configuration of different elements.

Atomic No.	Element	Electronic configuration	Atomic No.	Element	Electronic configuration
1	H	$1s^1$	16	S	– $3s^2\ 3p^4$
2	He	$1s^2$	17	Cl	– $3s^2\ 3p^5$
3	Li	$[He]^2\ 2s^1$	18	Ar	– $3s^2\ 3p^6$
4	Be	– $2s^2$	19	K	– $[Ar]^{18}\ 4s^1$
5	B	– $2s^2\ 2p^1$	20	Ca	– $4s^2$
6	C	– $2s^2\ 2p^2$	21	Sc	– $3d^1\ 4s^2$
7	N	– $2s^2\ 2p^3$	22	Ti	– $3d^2\ 4s^2$
8	O	– $2s^2\ 2p^4$	23	V	– $3d^3\ 4s^2$
9	F	– $2s^2\ 2p^5$	24	Cr*	– $3d^5\ 4s^1$
10	Ne	– $2s^2\ 2p^6$	25	Mn	– $3d^5\ 4s^2$
11	Na	$[Ne]^{10}\ 3s^1$	26	Fe	– $3d^6\ 4s^2$
12	Mg	– $3s^2$	27	Co	– $3d^7\ 4s^2$
13	Al	– $3s^2\ 3p^1$	28	Ni	– $3d^8\ 4s^2$
14	Si	– $3s^2\ 3p^2$	29	Cu*	– $3d^{10}\ 4s^1$
15	P	– $3s^2\ 3p^3$	30	Zn	– $3d^{10}\ 4s^2$

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Atomic No.	Element	Electronic configuration	Atomic No.	Element	Electronic configuration
31	Ga	– $3d^{10}\ 4s^2\ 4p^1$	72	Hf	– $4f^{14}\ 5d^2\ 6s^2$
32	Ge	– $3d^{10}\ 4s^2\ 4p^2$	73	Ta	– $4f^{14}\ 5d^3\ 6s^2$
33	As	– $3d^{10}\ 4s^2\ 4p^3$	74	W	– $4f^{14}\ 5d^4\ 6s^2$
34	Se	– $3d^{10}\ 4s^2\ 4p^4$	75	Re	– $4f^{14}\ 5d^5\ 6s^2$
35	Br	– $3d^{10}\ 4s^2\ 4p^5$	76	Os	– $4f^{14}\ 5d^6\ 6s^2$
36	Kr	– $3d^{10}\ 4s^2\ 4p^6$	77	Ir	– $4f^{14}\ 5d^7\ 6s^2$
37	Rb	– $[Kr]^{36}\ 5s^1$	78	Pt*	– $4f^{14}\ 5d^9\ 6s^1$
38	Sr	– $5s^2$	79	Au*	– $4f^{14}\ 5d^{10}\ 6s^1$
39	Y	– $4d^1\ 5s^2$	80	Hg	– $4f^{14}\ 5d^{10}\ 6s^2$
40	Zr	– $4d^2\ 5s^2$	81	Tl	– $4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$
41	Nb*	– $4d^4\ 5s^1$	82	Pb	– $4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$
42	Mo*	– $4d^5\ 5s^1$	83	Bi	– $4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$
43	Tc	– $4d^5\ 5s^2$	84	Po	– $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$
44	Ru*	– $4d^7\ 5s^1$	85	At	– $4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$
45	Rh*	– $4d^8\ 5s^1$	86	Rn	– $4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$
46	Pd*	– $4d^{10}$	87	Fr	– $[Rn]^{86}\ 7s^1$
47	Ag*	– $4d^{10}\ 5s^1$	88	Ra	– $7s^2$
48	Cd	– $4d^{10}\ 5s^2$	89	Ac	– $6d^1\ 7s^2$
49	In	– $4d^{10}\ 5s^2p^1$	90	Th	– $6d^2\ 7s^2$
50	Sn	– $4d^{10}\ 5s^2p^2$	91	Pa	– $5f^2 6d^1 7s^2$
51	Sb	– $4d^{10}\ 5s^2p^3$	92	U	– $5f^3 6d^1 7s^2$
52	Te	– $4d^{10}\ 5s^2p^4$	93	Np	– $5f^4 6d^1 7s^2$
53	I	– $4d^{10}\ 5s^2p^5$	94	Pu	– $5f^6 7s^2$
54	Xe	– $4d^{10}\ 5s^2p^6$	95	Am	– $5f^7 7s^2$
55	Cs	– $[Xe]^{54}\ 6s^1$	96	Cm	– $5f^7 6d^1 7s^2$
56	Ba	– $6s^2$	97	Bk	– $5f^9 7s^2$
57	La*	– $5d^1\ 6s^2$	98	Cf	– $5f^{10} 7s^2$
58	Ce*	– $4f^2\ 6s^2$	99	Es	– $5f^{11} 7s^2$
59	Pr	– $4f^3\ 6s^2$	100	Fm	– $5f^{12} 7s^2$
60	Nd	– $4f^4\ 6s^2$	101	Md	– $5f^{13} 7s^2$
61	Pm	– $4f^5\ 6s^2$	102	No	– $5f^{14} 7s^2$
62	Sm	– $4f^6\ 6s^2$	103	Lr	– $5f^{14} 6d^1 7s^2$
63	Eu	– $4f^7\ 6s^2$	104	Rf	– $5f^{14} 6d^2 7s^2$
64	Gd*	– $4f^7\ 5d^1\ 6s^2$	105	Ha	– $5f^{14} 6d^3 7s^2$
65	Tb	– $4f^9\ 6s^2$	106	Sg	– $5f^{14} 6d^5 7s^1$
66	Dy	– $4f^{10}\ 6s^2$	107	Bh	– $5f^{14} 6d^5 7s^2$
67	Ho	– $4f^{11}\ 6s^2$	108	Hs	– $5f^{14} 6d^6 7s^2$
68	Er	– $4f^{12}\ 6s^2$	109	Mt	– $5f^{14} 6d^7 7s^2$
69	Tm	– $4f^{13}\ 6s^2$	110	Ds	– $5f^{14} 6d^8 7s^2$
70	Yb	– $4f^{14}\ 6s^2$	111	Rg	– $5f^{14} 6d^{10} 7s^1$
71	Lu	– $4f^{14}\ 5d^1\ 6s^2$	112	Cn	– $5f^{14} 6d^{10} 7s^2$

* Elements with exceptional electronic configurations.

Electronic Configuration of Ions

The electronic configuration of the ions may be written almost similar to those of the atoms. In case of negatively charged ions, the extra electrons equal to the charge are added to the appropriate orbitals.

For example :

Cl (Z = 17) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$

Cl^- (Z = 17) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$

S (Z = 16) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$

S^{2-} (Z = 16) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$

In case of positively charged ions, the electrons equal to the charge on the ion are removed from the neutral atom. However, *it may be remembered that electrons with the highest value of n are removed first.* If more than one subshell of the valence shell are occupied, the one with the highest value of l loses the electron first. For example,

Mg (Z = 12) : $1s^2\ 2s^2\ 2p^6\ 3s^2$

Mg^{2+} (Z = 12) : $1s^2\ 2s^2\ 2p^6$

Fe (Z = 26) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

Fe^{2+} (Z = 26) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

It is very important to remember here that in case of Fe^{2+} ion, the electrons are removed from 4*s*-orbital first (highest value of n) and not from 3*d*-orbitals.

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Ni (Z = 28) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$

Ni^{2+} (Z = 28) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$

Co (Z = 27) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$

Co^{3+} (Z = 27) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

REMEMBER

While writing the electronic configuration of cations, the electronic configuration of the atom should be written first. Then the number of electrons equal to the units of positive charge should be removed from the outermost shell

SOLVED EXAMPLES

Example 52.

Which of the following are issoelectronic species : Na^+, K^+, Mg^{2+}, Ca^{2+}, S^{2-}, Ar ? **N.C.E.R.T.**

Solution : Isoelectronic species are those which contain same number of electrons

Na^+, Mg^{2+} are isoelectronic (contain 10 electrons)

K^+, Ca^{2+} S^{2-} and Ar are isolectronic (contain 18 electrons).

Example 53.

Write the electronic configuration of elements of atomic numbers 10, 17, 25, 29 and 37.

Solution : Electronic configuration of elements :

Atomic No. 10 : $1s^2\ 2s^2\ 2p^6$

Atomic No. 17 : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$

Atomic No. 25 : [Ar] $3d^5\ 4s^2$

Atomic No. 29 : [Ar] $3d^{10}\ 4s^1$

Atomic No. 37 : [Kr] $5s^1$

Example 54.

How many unpaired electrons are present in the ground state of (i) P (Z = 15) (ii) Fe^{2+} (Z = 26) (iii) Cl^- (Z = 17) ?

Solution : The number of unpaired electrons can be predicted by writing the electronic configurations :

(*i*) P (Z = 15) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$

$\therefore$ No. of unpaired electrons = 3

(*ii*) Fe^{2+} (Z = 26). The electronic configuration of Fe is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$. For Fe^{2+}, two electrons are removed from 4s-orbtial so that the configuration of Fe^{2+} is :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

All orbitals are completely filled except 3*d*-orbitals. The arrangement of five 3*d*-orbitals is :

↑↓	↑	↑	↑	↑

$\therefore$ No. of unpaired electrons = 4

(*iii*) Cl^- (Z = 17). The electronic configuration of Cl atom is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$. Cl^- ion has one extra electron and its configuration is :

$Cl^- : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Since all orbitals are filled, there is no unpaired electron.

Example 55.

What atoms are indicated by the following configuration ? Are they in the ground state or excited state ?

(*a*) $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$

(*b*) $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$

(*c*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1$

(*d*) $1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p_x^1\ 3p_y^1\ 3p_z^1\ 3d^1$

(*e*) $[Ar]\ 3d^5\ 4s^2$

Solution : (*a*) $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$. Atomic number is 9 and it is configuration of **fluorine** in ground state.

(*b*) $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$. Atomic number is 6 and it is configuration of **carbon** in excited state.

(*c*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1$ Atomic number is 14 and it is configuration of **silicon** in ground state.

(*d*) $1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p_x^1\ 3p_y^1\ 3p_z^1\ 3d^1$. Atomic number is 15 and it is configuration of **phosphorus** in excited state.

(*e*) [Ar] $3d^5\ 4s^2$. Atomic number is 25 and it is configuration of **manganese** in ground state.

Example 56.

Give the symbol of the atom whose ground state corresponds to each of the following configurations:

(*i*) $1s^2\ 2s^2\ 2p^6$

(*ii*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Give two examples of negative and two positive ions corresponding to the above configurations.

Solution : (*i*) $1s^2\ 2s^2\ 2p^6$. Atomic number is 10 and it corresponds to Ne (neon).

The ions corresponding to this configuration are :

O^{2-}, F^-, Na^+, Mg^{2+}.

(*ii*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$. Atomic number is 18 and it corresponds to Ar (argon).

The ions corresponding to this configuration are :

S^{2-}, Cl^-, K^+, Ca^{2+}.

Example 57.

Write the electronic configuration of the following ions :

(*i*) H^- (*ii*) Na^+ (*iii*) O^{2-} (*iv*) F^- **N.C.E.R.T.**

Solution :

(*i*) $1s^2$

(*ii*) $1s^2\ 2s^2\ 2p^6$

(*iii*) $1s^2\ 2s^2\ 2p^6$

(*iv*) $1s^2\ 2s^2\ 2p^6$

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Example 58.

The quantum numbers of six elements are given below. Arrange them in order of increasing energies. If any of these combinations has/have the same energies, list them.

(1) $n = 4, \quad l = 2, \quad m_l = -2, \quad m_s = -\frac{1}{2}$

(2) $n = 3, \quad l = 2, \quad m_l = 1, \quad m_s = +\frac{1}{2}$

(3) $n = 4, \quad l = 1, \quad m_l = 0, \quad m_s = +\frac{1}{2}$

(4) $n = 3, \quad l = 2, \quad m_l = -2, \quad m_s = -\frac{1}{2}$

(5) $n = 3, \quad l = 1, \quad m_l = -1, \quad m_s = +\frac{1}{2}$

(6) $n = 4, \quad l = 1, \quad m_l = 0, \quad m_s = +\frac{1}{2}$

N.C.E.R.T.

Solution : $5(3p) < 2\,(3d) = 4\,(3d) < 6\,(4p) = 3\,(4p) < 1\,(4d)$

Example 59.

Indicate the number of unpaired electrons in (i) P (ii) Si (iii) Cr (iv) Fe (v) Kr

N.C.E.R.T.

Solution :

(i) P(Z = 15) : [Ne] $3s^2\,3p^3$
unpaired electrons = 3

(ii) Si (Z = 16) : [Ne] $3s^2 3p^2$
unpaired electrons = 2

(iii) Cr (Z = 24) : [Ar] $3d^5\,4s^1$
unpaired electrons = 6

(iv) Fe (Z = 26) : [Ar] $3d^6 4s^2$
unpaired electrons = 4

(v) Kr (Z = 36) : [Ar] $3d^{10} 4s^2\,4p^6$
unpaired electrons = 0.

Example 60.

Which of the following do and which do not make sense ?

$7p,\ 2d,\ 3s^3,\ 3p_y^3,\ 4f.$

Solution :

$7p$: makes sense

$2d$: does not make sense. (There are no d-orbitals for $n = 2$)

$3s^3$: does not make sense (3s-orbital cannot have more than two electrons)

$3p_y^3$: does not make sense ($3p_y$ orbital cannot have more than two electrons)

$4f$: makes sense

Example 61.

An atom has 2 electrons in the first (K) shell, 8 electrons in the second (L) shell and 2 electrons in the third (M) shell. Give its electronic configuration and find out the following :

(a) Atomic number

(b) Total number of principal quantum numbers

(c) Total number of sublevels

(d) Total number of s-orbitals

(e) Total number of p-electrons.

Solution : The electronic configuration of the atom is :

$1s^2\,2s^2\,2p^6\,3s^2$

(a) Atomic number = 2 + 2 + 6 + 2 = 12

(b) Number of principal quantum numbers = 3

(c) Number of sub-levels = 4 (1s, 2s, 2p, 3s)

(d) Number of s-orbitals = 3 (1s, 2s, 3s)

(e) Total number of p-electrons = 6.

Example 62.

What is the maximum number of unpaired electrons in Cu (Z = 29), Br^- (Z = 35) and K^+ (Z = 19) ?

Solution :

Cu (Z = 29) : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$
Unpaired electrons = 1

Br (Z = 35) : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^5$

$\therefore$ Br^- (36e) : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6$
Unpaired electrons = 0

K (Z = 19) : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$

K^+ (18 e) : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$
Unpaired electrons = 0

Practice Problems

54. How many unpaired electrons are present in the ground state of phosphorus (Z = 15) ?

55. Name the elements which correspond to each of the following configurations :

(a) $1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$

(b) $1s^2\,2s^2\,2p^6\,3s^2\,3p_x^1$

(c) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$

(d) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^1$

56. List the values of n and l for the following orbitals:

(a) 3s (b) 4p (c) 4f (d) 3d

57. Write down all the four quantum numbers for outermost electron of sodium atom (Z = 11).

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58. What is the maximum number of electrons that may be present in all the atomic orbitals with principal quantum number 3 and azimuthal quantum number 2 ?

59. Write down the values of all the quantum numbers for 19th electron of Cr (Z = 24).

60. How many electrons in zinc (Z = 30) have $n + l$ value equal to 4 ?

61. Write the electronic configuration of chromium (Z = 24) and predict in it

(*i*) number of subshells

(*ii*) number of electrons in subshell having $l = 0$

(*iii*) number of electrons having $n + l$ value equal to 3

(*iv*) number of electrons in highest value of n.

62. How many electrons in p-subshell of argon (Z = 18) have same spin ?

Answers to Practice Problems

54. Three

55. (*a*) Oxygen (*b*) Aluminium
(*c*) Potassium (*d*) Chromium.

56. (*a*) $n = 3, l = 0$ (*b*) $n = 4, l = 1$
(*c*) $n = 4, l = 3$ (*d*) $n = 3, l = 2$

57. $n = 3, l = 0, m = 0, s = +½$

58. Ten.

59. $n = 4, l = 0, m = 0, s = +½$

60. 8 (electrons in 4*s* and 3*p*-subshells)

61. (*i*) 7 (*ii*) 7 (*iii*) 8 (*iv*) 1

62. 6

Hints & Solutions on page 68

add on

Conceptual Questions 2

CONCEPTUAL QA

Q. 1. What will happen to the wavelength associated with a moving particle if its velocity is reduced to half?

Ans. Wavelength becomes double of the original value because $\lambda = \frac{h}{mv}$ or $\lambda \propto \frac{1}{v}$.

Q. 2. Can we apply Heisenberg's uncertainty principle to a stationary state ?

Ans. No, because velocity is zero and position can be measured accurately.

Q. 3. An electron beam after hitting a nickel crystal produces a diffraction pattern. What do you conclude ?

Ans. Electron has wave nature.

Q. 4. A molecule of O_2 and O_3 travel with the same velocity. What is the rates of their wavelength ?

Ans. $\lambda = \frac{h}{mv}$ or $\lambda \propto \frac{1}{m}$.

Mass of O_2 molecule is 32 u and mass of O_3 molecule is 48 u.

$\therefore \frac{\lambda(O_2)}{\lambda(O_3)} = \frac{48}{32} = 1.5 \quad \therefore \quad \lambda(O_2) = 1.5$ times $\lambda\,(O_3)$.

Q. 5. What is the sequence of energies of 4*s*, 4*p*, 4*d* and 4*f*-orbitals in (*i*) a hydrogen atom and (*ii*) a zinc atom?

Ans. (*i*) $4s = 4p = 4d = 4f$ (*ii*) $4s < 4p < 4d < 4f$.

Q. 6. Which shell would be the first to have a *g*-subshell ?

Ans. 5th energy shell.

Q. 7. The 4*f* subshell of an atom contains 12 electrons. What is the maximum number number of electrons having same spin in it ?

Ans. Seven.

Q.8. Which of the following sets of quantum numbers for orbitals in hydrogen atom has larger energy ?

$n = 3, l = 2, m_l = +1$, $n = 3, l = 2, m_l = -1$

Ans. Both are orbitals of the same subshell and, therefore, have same energy.

Q.9. How many nodes are present in 3p-orbital ?

Ans. No. of nodes in an orbital = $(n - l - 1)$

$\therefore$ No. of nodes in 3*p*-orbital = 3 – 1 – 1 = 1.

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Q.10. What is the difference in the angular momentum of an electron present in 2*p* and that present in 3*p*-orbital ?

Ans. Angular momentum is same because it depends upon the quantum number l and not on n as :

Angular momentum = $\frac{h}{2\pi}\sqrt{l(l+1)}$.

Q.11. What will be the maximum number of electrons present in an atom having $n + l = 4$?

Ans. The subshells which can have n + l = 4 are 4 *s* (4 + 0) and 3p (3 + 1). Therefore, these will accommodate maximum of 2 + 6 = 8 electrons.

Q.12. How many spherical nodes do you expect in a 4*s*-orbital ?

Ans. Three nodes.

Q.13. What is the maximum number of electrons which can be accommodated in an atom in which the highest principal quantum number value is 4 ?

Ans. 36 corresponding to Kr ($4s^2\ 4p^6$).

Q.14. How many quantum numbers are required to specify an orbital ?

Ans. Three (n, l and m_l)

Q.15. What are the quantum numbers of the valence electrons in potassium atom (Z = 19)in ground state ?

Ans. For 3p-orbital,

$n = 4, l = 0, m_l = 0, m_s = +\frac{1}{2}$.

Q.16. In which atom, the outermost electron can have the following set of quantum numbers ?

$\boldsymbol{n = 3, l = 0, m_l = 0\ m_s = -\frac{1}{2}}$

Ans. Sodium.

Q.17. What is the value of orbital angular momentum for an electron in 2*s*-orbital ?

Ans. Angular momentum is given as $\frac{h}{2\pi}\sqrt{l\,(l+1)}$

Since for 2*s* orbital, $l = 0$ ∴ Angular momentum = 0

Q.18. How many unpaired electrons are present in P(Z = 15) ?

Ans. Electronic configuration of P is : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

No. of unpaired electrons = 3.

Q.19. In what ways do the spatial distribution of the orbitals in 1s and 2s differ ?

Ans. 2s orbital is larger while 1*s* orbital is smaller. 2*s* orbit has a sperical node while 1s orbital does not have.

Q. 20. Explain the meaning of the symbol $4d^6$. ***N.C.E.R.T.***

Ans. It means that 4d subshell has 6 electrons. 4 represents fourth energy shell and *d* is a subshell and 6 electrons are present in *d* orbitals of subshell.

Q. 21. How many nodes are present in 4d orbital ?

Ans. No. of nodes = $(n - l - 1) = 4 - 2 - 1 = 1$ (one node).

Q. 22. What is the lowest shell which has an *f*-subshell ?

Ans. Fourth

Q. 23. Which quantum number does not follow from the solutions of Schrodinger wave equation ?

Ans. Spin quantum number

Q. 24. What is value of angular momentum for an electron in 5th orbit according to Bohr's theory?

Ans. $\frac{5h}{2\pi}$.

Q. 25. How are d_{xy} and $d_{x^2-y^2}$ orbitals related ?

Ans. The d_{xy} orbital is exactly like $d_{x^2-y^2}$ orbital except that its lobes are at an angle of 45° to the lobes of $d_{x^2-y^2}$ orbital.

Q. 26. How many electrons are possible in all shells with $n + l = 5$?

Ans. Subshell with $n + l = 5$ are 5s, 4*p* and 3*d*. Hence electrons present in these subshells are 2 + 6 + 10 = 18.

Q. 27. Write n, l and m_l values for
(*i*) 3s (*ii*) $2p_y$ (*iii*) $4p_z$.

Ans. (*i*) $n = 3, l = 0, m_l = 0$ (*ii*) $n = 2, l = 1, m_l = +1$ or -1 (*iii*) $n = 4$, l = 1, $m_l = 0$

Q. 28. Does d_z^2 orbital has zero electron density in *xy* plane ?

Ans. No. d_z^2 orbital has electron density in *xy* plane also as shown by ring.

CONCEPTUAL QA

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Q. 29. Which of the four qunatum numbers (n, l, m_l, m_s) determine
(a) the energy of an electon in a hydrogen atom and multi electron atoms
(b) the size of an orbital
(c) the shape of an orbital
(d) the orientation of an orbital in space ? ***N.C.E.R.T.***

Ans. (a) n (b) n (c) l (d) m_l.

Q. 30. What physical meaning is attributed to the square of the absolute value of wave function $|\Psi^2|$? ***N.C.E.R.T.***

Ans. It measures the electron probability density at a point in an atom.

Q. 31. Discuss the similarities and differences between a 1*s* and a 2*s* orbital.

Ans. **Similarities.** (*i*) Both the orbitals have spherical shape.
(*ii*) Both have same angular momentum (equal to zero).
Differences. (*i*) Size of 2*s* orbital is larger than that of 1*s* orbital
(*ii*) 1s has no node while 2s has one node.
(*iii*) Energy of 2*s* orbital is more than that of 1*s*.

Q. 32. What is the difference between the notation *l* and L ?

Ans. The notation l represents azimuthal quantum number, which can have values 0, 1, 2, ... etc. whereas L represents second Bohr orbit for which $n = 2$.

Q. 33. How many electrons in an atom may have the following quantum number ?
(i) $n = 4, m_s = +½$ (ii) $n = 3, l = 0$

Ans. (*i*) $n = 4$, $m_s = +½ = 16$ electrons
(*ii*) $n = 3, l = 0 = 2$

Q. 34. For each of the following pair of hydrogen orbitals, indicate which is higher in energy :
(i) 1*s*, 2*s* **(ii) 2*p*, 3*p***
(iii) $3d_{xy}$, $3d_{yz}$ **(iv) 3*s*, 3*d***
(v) 4*f*, 5*s*. ***N.C.E.R.T.***

Ans. (*i*) 2*s* (*ii*) 3*p* (*iii*) both have same energy (*iii*) both have same energy (*v*) 5*s*.

Q. 35. Which orbital in each of the following pairs is lower in energy in a many electron atom ?
(i) 2*s*, 2*p* **(ii) 3*p*, 3*d***
(iii) 3*s*, 4*s* **(iv) 4*d*, 5*f*** ***N.C.E.R.T.***

Ans. (*a*) 2*s* (*b*) 3*p* (*c*) 3*s* (*d*) 4*d*.

Q. 36. Nickel atom can lose two electrons to form Ni^{2+} ion. The atomic number of nickel is 28. From which orbital will nickel lose two electrons ?

Ans. The electronic configuration of nickel is
Ni : [Ar] $3d^8 4s^2$
It will lose two electrons from 4*s* orbital.

Q.37. Which of the following orbitals are degenerate ?
$3d_{xy}$, $4d_{xy}$, $3d_{z^2}$, $3d_{yz}$, $4d_{yz}$, $4d_{z^2}$

Ans. The degenerate orbitals are :
$3d_{xy}$, $3d_{z^2}$, $3d_{yz}$, and $4d_{xy}$, $4d_{yz}$, $4d_{z^2}$

Q.38. Calculate the total number of angular nodes and radial nodes present in 3*p* orbital.

Ans. For 3*p* orbital, $n = 3$ and $l = 1$
No. of radial nodes = $n - l - 1 = 3 - 1 - 1 = 1$
No. of angular nodes = $l = 1$

Q.39. (*a*) Based on Bohr Bury's rules arrange the following orbitals in the increasing order of energy.
(i) 1*s*, 2*s*, 3*s*, 2*p*
(ii) 4*s*, 3*s*, 3*p*, 4*d*
(iii) 5*p*, 4*d*, 5*d*, 4*f*, 6*s*
(iv) 5*f*, 6*d*, 7*s*, 7*p*
(*b*) Based on these rules solve the questions given below :
(i) Which of the following orbitals has the lowest energy ?
4*d*, 4*f*, 5*s*, 5*p*
(ii) Which of the following orbitals has the highest energy ?
5*p*, 5*d*, 5*f*, 6*s*, 6*p*

Ans. (*a*) (*i*) $1s < 2s < 2p < 3s$ (*ii*) $3s < 3p < 4s < 4d$ (*iii*) $4d < 5p < 6s < 4f < 5d$ (*iv*) $7s < 5f < 6d < 7p$
(*b*) (*i*) 5*s* has lowest energy (*ii*) 5*f* has highest energy.

CONCEPTUAL QA

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Problem 9. **When would the wavelength associated with an electron become equal to the wavelength associated with proton? (Mass of electron = 9.1095×10^{-31} kg, mass of proton = 1.6725×10^{-27} kg).**

Solution According to de-Broglie equation,

$$\lambda_e = \frac{h}{mv}$$

For electron, $\lambda_e = \frac{h}{m_e v_e}$

For proton, $\lambda_p = \frac{h}{m_p v_p}$

But $\lambda_e = \lambda_p$

$\therefore \quad \frac{h}{m_e v_e} = \frac{h}{m_p v_p}$

or $m_e v_e = m_p v_p$

or $v_e = \frac{m_p v_p}{m_e}$

$$= \frac{1.6725 \times 10^{-27}}{9.1095 \times 10^{-31}} \times v_p = 1836 v_p$$

Velocity of electron = 1836 velocity of proton.

Problem 10. **Calculate the ratio between the wavelength of an electron and a proton if the proton is moving with half the velocity of electron. (mass of electron = 9.11×10^{-31} kg, mass of proton = 1.67×10^{-27} kg).**

Solution $\lambda = \frac{h}{m_e v_e}, \lambda_p = \frac{h}{m_p v_p}$

$$\frac{\lambda_e}{\lambda_p} = \frac{m_p v_p}{m_e v_e}, \quad v_p = \frac{1}{2} v_e \text{ or } \frac{v_p}{v_e} = \frac{1}{2}$$

$$\frac{\lambda_e}{\lambda_p} = \frac{1\, m_p}{2\, m_e} = \frac{1}{2} \times \frac{1.67 \times 10^{-27}}{9.11 \times 10^{-31}} = 916.6.$$

Problem 11. **Find out the number of waves made by a Bohr electron in one complete revolution in its 3rd orbit.**

Solution In general, the number of waves in any orbit is

$$\text{Number of waves} = \frac{\text{Circumference of orbit}}{\text{Wavelength}}$$

$$= \frac{2\pi r}{\lambda}$$

But $\lambda = \frac{h}{mv}$

$$\text{No. of waves} = \frac{2\pi r}{h/mv} = \frac{2\pi r . mv}{h}$$

or $$= \frac{2\pi (mvr)}{h}$$

The angular momentum of Bohr's 3rd orbit is

$$mvr = \frac{3h}{2\pi}$$

$$\therefore \quad \text{No. of waves} = \frac{2\pi}{h} \times \frac{3h}{2\pi} = 3$$

No. of waves in Bohr's 3rd orbit = 3.

Problem 12. **An electron in a H-atom in its ground state absorbs 1.50 times as much energy as the minimum energy required for it to escape from the atom. What is the wavelength of the emitted electron?**

Solution The energy required to remove an electron from H atom = Ionisation energy of H atom

$$= 2.18 \times 10^{-18} \text{ J atom}^{-1}$$

The amount of energy absorbed $= 1.50 \times 2.18 \times 10^{-18}$ J

$$= 3.27 \times 10^{-18} \text{ J}$$

Amount of energy converted to kinetic energy

$$= 3.27 \times 10^{-18} - 2.18 \times 10^{-18} \text{ J}$$

$$= 1.09 \times 10^{-18} \text{ J}$$

$$\text{K.E} = \frac{1}{2} m v^2$$

$$v = \sqrt{\frac{2\,\text{K.E}}{m}} = \sqrt{\frac{2 \times (1.09 \times 10^{-18}\text{J})}{(9.1 \times 10^{-31}\text{kg})}}$$

$$= 1.55 \times 10^{6} \text{ ms}^{-1}$$

According to de-Broglie equation,

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.63 \times 10^{-34} \text{ Js}}{(9.1 \times 10^{-31} \text{ kg}) \times (1.55 \times 10^{6} \text{ ms}^{-1})}$$

$$= \mathbf{4.70 \times 10^{-10} m}$$

Solution File Hints & Solutions for Practice Problems

1. (*i*) p = Atomic no. = 6

Mass number = $p + n$

$12 = 6 + n \quad \therefore n = \mathbf{6}$

(*ii*) p = Atomic no. = **26**

$n + p$ = Mass no.

$n + 26 = 56 \quad \therefore n = \mathbf{30}$

(*iii*) p = atomic no. = **38**

$n + p$ = Mass no.

$n + 38 = 88 \quad \therefore n = \mathbf{50}$

(*iv*) p = atomic no = 92

$n + p = 238$

$\therefore \quad n = 238 - 92 = \mathbf{146.}$

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Solution File

8. Since it carries – 1 charge, it will have one electron more than the number of protons.
Let number of electrons = x

No. of protons = $x - 1$

No. of neutrons = $x + x \times \frac{11.1}{100} = 1.111\,x$

Now, $x - 1 + 1.111\,x = 37$

or $2.111x = 38$

$x = 18$

No. of e = 18

No. of p = 18 – 1 = 17

No. of n = 35 – 17 = 18

Symbol $^{35}_{17}Cl^-$

9. $\nu = \frac{c}{\lambda}$

$= \frac{3.0\times10^8}{460\times10^{-9}} = \mathbf{6.52 \times 10^{14}\ sec^{-1}}$

10. Frequency, $\nu = 980\ kHz = 980 \times 10^3\ s^{-1}$

Wavelength $\lambda = \frac{c}{\nu}$

$\therefore \quad \lambda = \frac{3.0\times10^8\ ms^{-1}}{1368\times10^3\ s^{-1}} = \mathbf{306\ m.}$

11. Wave number, $\overline{\nu} = \frac{\nu}{c}$

$\therefore \quad \overline{\nu} = \frac{4\times10^{14}\ s^{-1}}{3.0\times10^8 ms^{-1}}$

$= \mathbf{1.33 \times 10^6\ m^{-1}.}$

12. Frequency, $\nu = \frac{c}{\lambda}$

$\therefore \quad \nu = \frac{3.0\times10^8 ms^{-1}}{480\times10^{-9} m}$

$= \mathbf{6.25 \times 10^{14}\ s^{-1}}$

Wave number, $\overline{\nu} = \frac{1}{\lambda}$

$= \frac{1}{480\times10^{-9}}$

$= \mathbf{2.08 \times 10^6\ m^{-1}}$

13. (*i*) Wave number, $\overline{\nu} = \frac{1}{5800\times10^{-10} m}$

$= 1.724 \times 10^6\ m^{-1}$

(*ii*) Frequency, $\nu = \frac{c}{\lambda} = \frac{3.0\times10^8 ms^{-1}}{5800\times10^{-10} m}$

$= \mathbf{5.172 \times 10^{14}\ s^{-1}}$

14. Wavelength, $\lambda = 25.0\ \mu m = 25.0 \times 10^{-6}\ m$

Frequency, $\nu = \frac{c}{\lambda} = \frac{3.0\times10^8\ ms^{-1}}{25.0\times10^{-6} m}$

$= \mathbf{1.2 \times 10^{13}\ Hz}$

Wave number, $\overline{\nu} = \frac{1}{\lambda} = \frac{1}{25.0\times10^{-6} m}$

$= \mathbf{4.0 \times 10^4\ m}$

15. (*i*) $E = h\nu = \frac{hc}{\lambda}$

$\therefore \quad E = \frac{6.63\times10^{-34}\times3.0\times10^8}{0.50\times10^{-10}}$

$= 3.98 \times 10^{-15}\ J$

(*ii*) $E = 6.63 \times 10^{-34}\ Js \times 3 \times 10^{15}\ s^{-1}$

$= \mathbf{1.98 \times 10^{-18}\ J}$

16. $\lambda = 25.0\ \mu m = 25.0 \times 10^{-6}\ m$

$\nu = \frac{c}{\lambda} = \frac{3.0\times10^8}{25.0\times10^{-6}} = 1.2 \times 10^{13}$

Energy of photon,

$E = h\nu = 6.626 \times 10^{-34} \times 1.2 \times 10^{13}$

$= \mathbf{7.96 \times 10^{-21}\ J}$

17. Energy of photon,

$E = \frac{hc}{\lambda}$

$\therefore \quad E = \frac{(6.63\times10^{-34}\ Js)\times(3\times10^8\ ms^{-1})}{400\times10^{-9}\ m}$

$= 4.97 \times 10^{-19}\ J$

No. of photons in 1J

$= \frac{1}{4.97\times10^{-19}} = \mathbf{2.01 \times 10^{18}\ photons}$

18. Wavelength of light,

$\lambda = 250\ nm = 250 \times 10^{-9}\ m$

$E = \frac{6.63\times10^{-34}\times3.0\times10^8}{250\times10^{-9}}$

$= 7.956 \times 10^{-19}\ J$

Energy required per molecule

$= 9.6 \times 10^{-17}\ J$

No. of photons per molecule

$= \frac{9.6\times10^{-17}}{7.956\times10^{-19}} = \mathbf{121\ photons}$

19. K.E. $= h\nu - h\nu_0 = h\,(\nu - \nu_0)$

$h = 6.63 \times 10^{-34}\ Js,$

$\upsilon = 1.0 \times 10^{15}\ s^{-1}, \upsilon_0 = 7.0 \times 10^{14}\ s^{-1}$

$\therefore$K.E. $= 6.63 \times 10^{-34}\,(10.0 \times 10^{14} - 7.0 \times 10^{14})$

$= 6.63 \times 10^{-34} \times 3.0 \times 10^{14} = \mathbf{1.99 \times 10^{-19}\ J}$

$= \mathbf{3.44 \times 10^{-22}\ J}$

20. K.E. $= h\nu - h\nu_0$

If the velocity is zero, K.E. = 0

$\therefore \quad 0 = h\nu - h\nu_0$

or $h\nu = h\nu_0$ or $\nu = \nu_0$

$\therefore \quad \nu = \frac{c}{\lambda} = \frac{3.0\times10^8 ms^{-1}}{6800\times10^{-10} m}$

$= \mathbf{4.41 \times 10^{14}\ s^{-1}}$

Threshold frequency = $4.41 \times 10^{14}\ s^{-1}$

Work function = $h\nu_0 = 6.626 \times 10^{-34} \times 4.41 \times 0^{14}$

$= \mathbf{2.92 \times 10^{-19}\ J}$

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Solution File

© 21. $\frac{1}{\lambda} = 109678\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)\text{ cm}^{-1}$

For Balmer series,

$n_1 = 2,$

$\frac{1}{\lambda} = 109678\left(\frac{1}{2^2}-\frac{1}{n^2}\right)\text{cm}^{-1}$

For the first line,

$n_2 = 3$ so that

$\frac{1}{\lambda} = 109678\left(\frac{1}{4}-\frac{1}{9}\right)\text{ cm}^{-1}$

$= 109678 \times \frac{5}{36}$

or $\lambda = \frac{36}{5\times109678}\text{ cm} = 6.56\times10^{-5}\text{ cm}$

$= \mathbf{656\text{ nm}}$

For the limiting line,

$n_2 = \infty$

$\therefore \frac{1}{\lambda} = 109678\left(\frac{1}{2^2}-\frac{1}{\infty^2}\right)\text{ cm}^{-1}$

$= 109678 \times \frac{1}{4}$

or $\lambda = \frac{4}{109678}\text{ cm} = 3.647\times10^{-5}\text{ cm}$

$= \mathbf{364.7\text{ nm.}}$

© 22. $\frac{1}{\lambda} = 109678\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)\text{ cm}^{-1}$

$\therefore \frac{1}{\lambda} = 109678\left(\frac{1}{1^2}-\frac{1}{3^2}\right)\text{ cm}^{-1} = 109678\times\frac{8}{9}$

or $\lambda = \frac{9}{109678\times8}\text{ cm} = 102.6\times10^{-7}\text{ cm}$

$= \mathbf{102.6\text{ nm}}$

© 23. According to Rydberg equation,

$\frac{1}{\lambda} = 109678\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$

Here $n_1 = 1, n_2 = \infty$

$\therefore \frac{1}{\lambda} = 109678\left(\frac{1}{1^2}-\frac{1}{\infty^2}\right)$

$\frac{1}{\lambda} = 109678$

or $\lambda = \frac{1}{109678} = 9.11\times10^{-6}\text{ cm}$

or $= \mathbf{9.11\times10^{-8}\text{ m}}$

Now, $E = \frac{6.63\times10^{-34}\times3.0\times10^{8}}{9.11\times10^{-8}}$

$= \mathbf{2.183\times10^{-18}\text{ J}}$

© 24. For Balmer series, the longest wavelength corresponds to transition from $n = 3$ to $n = 2$

$\bar{\nu} = 109678\left(\frac{1}{2^2}-\frac{1}{n^2}\right)\text{ cm}^{-1}$

$= 109678\left(\frac{1}{2^2}-\frac{1}{3^2}\right)$

$= 15233.0\text{ cm}^{-1}$

or $= \mathbf{1.523\times10^{6}\text{ m}^{-1}}$

© 25. No. of lines produced when an electron in 6th shell drops to ground state

$\frac{(n_2-n_1)(n_2-n_1+1)}{2} = \frac{(6-1)\times(6-1+1)}{2}$

$= \frac{5\times6}{2} = 15\text{ lines}$

These lines correspond to

$6\to5, 6\to4, 6\to3, 6\to2, 6\to1$ (5 lines)

$5\to4, 5\to3, 5\to2, 5\to1$ (4 lines)

$4\to3, 4\to2, 4\to1$ (3 lines)

$3\to2, 3\to1$ (2 lines)

$2\to1$ (1 line)

© 26. $\upsilon = \frac{\Delta E}{h} = \frac{399.1\text{ kJ mol}^{-1}}{3.98\times10^{-13}} = \mathbf{1\times10^{15}\text{ Hz}}$

Now, $\lambda = \frac{c}{\nu} = \frac{3.0\times10^{8}\text{ msec}^{-1}}{1\times10^{15}\text{ sec}^{-1}} = 3.0\times10^{-7}\text{ m}$

$= \mathbf{300\text{ nm}}$

© 27. $E_n = -\frac{2.18\times10^{-18}}{n^2}\text{ J atom}^{-1}$

For ionization from 5th orbit,

$n_1 = 5$ and $n_2 = \infty$

$= 2.18\times10^{-18}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$

$= 2.18\times10^{-18}\left(\frac{1}{5^2}-\frac{1}{\infty}\right) = \mathbf{8.72\times10^{-20}\text{ J}}$

For ionization of H atom,

$n_1 = 1, n_2 = \infty$

$\Delta E = 2.18\times10^{-18}\left(\frac{1}{1^2}-\frac{1}{\infty}\right)$

$= \mathbf{2.18\times10^{-18}\text{ J}}$

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28. $\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

For spectral line of electron jump from $n = 5$ to $n = 3$,

$$\frac{1}{1281.8} = R\left(\frac{1}{3^2} - \frac{1}{5^2}\right) = R\left(\frac{16}{225}\right) \quad ...(i)$$

For spectral line of electron jump from $n = 3$ to $n = 1$

$$\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{3^2}\right) = R\left(\frac{8}{9}\right) \quad ...(ii)$$

Dividing (i) by (ii)

$$\frac{\lambda}{1281.8} = \frac{16}{225} \times \frac{9}{8}$$

or $$\lambda = \frac{16 \times 9}{225 \times 8} \times 1281.8 = \mathbf{102.5\ nm}$$

29. $$\bar{\nu} = \frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For He^+ spectrum, $Z = 2$, $n_2 = 4$, $n_1 = 2$

$$\bar{\nu} = \frac{1}{\lambda} = R_H \times 4 \left(\frac{1}{2^2} - \frac{1}{4^2}\right) = \frac{3R_H}{4}$$

For hydrogen spectrum, $\frac{1}{\lambda} = \frac{3R_H}{4}$

$$\therefore \quad \bar{\nu} = \frac{1}{\lambda} = R_H \times 1 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{3R_H}{4}$$

$$\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$

$$\therefore \quad n_1 = 1, n_2 = 2$$

Thus, the transition is from $n = 2$ to $n = 1$.

30. Ionisation energy is the energy needed when an electron is removed from $n_1 = 1$ to $n_2 = \infty$. For H-atom,

$$\text{I. E.} = \frac{2\pi^2 me^4}{n^2 h^2}$$

Since $n = 1$

$$\therefore \quad \text{I.E.} = \frac{2\pi^2 me^4}{h^2} = 13.6\ \text{eV}$$

Ionisation energy of H like ion,

$$\text{I. E} = \frac{2\pi^2 me^4 Z^2}{h^2}$$

I.E. for He^+ ion $(Z = 2)$ = I.E. for H – atom $\times (2)^2$

$= 13.6 \times 4 = \mathbf{54.4\ eV}$

Similarly, I.E. for Li^{2+} ion $(Z = 3)$ = I.E. for H-atom $\times (3)^2$

$= 13.6 \times 9 = \mathbf{122.4\ eV}$

31. $\Delta E = 2.18 \times 10^{-18}\left(\frac{1}{1^2} - \frac{1}{5^2}\right) = \mathbf{2.09 \times 10^{-18} J}$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^8}{2.09 \times 10^{-18}}$$

$= 9.51 \times 10^{-8}\ \text{m} = \mathbf{951\ Å}$

32. $$\bar{\nu} = 109678\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For longest wavelength, $n_2 = 3$, $n_1 = 2$

$$\bar{\nu} = 109678\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$= 109678 \times \frac{5}{36} = 1.523 \times 10^4\ \text{cm}^{-1}$$

$$= \mathbf{1.523 \times 10^6\ m^{-1}}$$

33. $$E_i = -\frac{2.18 \times 10^{-18}}{2^2} = 5.45 \times 10^{-19}\ \text{J}$$

$$E_f = 0$$

$$\Delta E = 0 - (-5.45 \times 10^{-19}) = 5.45 \times 10^{-19}\ \text{J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^8}{5.45 \times 10^{-19}}$$

$= 3.647 \times 10^{-7}$ or $\mathbf{3647\ Å}$

34. $$\lambda = \frac{6.626 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{0.1\ \text{kg} \times 10\ \text{ms}^{-1}}$$

$= \mathbf{6.626 \times 10^{-34} m}$

35. $$\lambda = \frac{h}{mv} \text{ or } m = \frac{h}{\lambda v}$$

$$= \frac{6.63 \times 10^{-34}}{3.6 \times 10^{-10} \times 3.0 \times 10^8} = \mathbf{6.139 \times 10^{-33}\ kg}$$

36. $$mv = \frac{h}{\lambda}$$

$$= \frac{6.63 \times 10^{-34}\ \text{kgm}^2\text{s}^{-1}}{0.1 \times 10^{-9}\ \text{m}}$$

$= \mathbf{6.63 \times 10^{-24}\ kg\ ms^{-1}}$

37. Mass of α-particle $= \frac{4}{6.022 \times 10^{23}} = 6.64 \times 10^{-24}\ g$

or $= 6.64 \times 10^{-24} \times 10^{-3}\ \text{kg} = 6.64 \times 10^{-27}\ \text{kg}$

$$\lambda = \frac{h}{mv} \quad \text{or} \quad v = \frac{h}{m\lambda}$$

$\lambda = 12\ \text{pm} = 12 \times 10^{-12}\ \text{m}$

$h = 6.63 \times 10^{-34}\ \text{Js}$

$$v = \frac{6.63 \times 10^{-34}}{6.64 \times 10^{-27} \times 12 \times 10^{-12}}$$

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$= 8.32 \times 10^3\ ms^{-1}$

K.E. $= \frac{1}{2}mv^2 = \frac{1}{2} \times 6.64 \times 10^{-27} \times (8.32 \times 10^3)^2$

$= \mathbf{2.30 \times 10^{-19}\ J}$

© 38. $\lambda = \frac{h}{mv}$

$= \frac{6.63 \times 10^{-34}}{0.1 \times 4.37 \times 10^{-5}} = \mathbf{1.52 \times 10^{-38} m}$

© 39. The kinetic energy of the electron is provided by accelerating potential

$\frac{1}{2}mv^2 = eV \quad or \quad v = \left(\frac{2Ve}{m}\right)^{\frac{1}{2}}$

$\therefore \quad \lambda = \frac{h}{mv} = \frac{h}{m\left(2Ve/m\right)^{\frac{1}{2}}} = \frac{h}{(2Vem)^{\frac{1}{2}}}$

$\therefore \quad (2Vem)^{1/2} = \frac{h}{\lambda} \quad or \quad 2Vem = \frac{h^2}{\lambda^2}$

or $V = \frac{h^2}{\lambda^2 \times 2 \times e \times m}$

$\lambda = 9\ pm = 9 \times 10^{-12}\ m,$
$e = 1.6 \times 10^{-19}\ C,$
$m = 9.1 \times 10^{-31}\ kg$
$h = 6.63 \times 10^{-34}\ Js$

$$V = \frac{(6.63 \times 10^{-34}\ Js)^2}{(9 \times 10^{-12}\ m)^2 \times 2 \times (1.6 \times 10^{-19} C) \times 9.1 \times 10^{-31} kg}$$

$= 1.86 \times 10^4\ kg\ m^2\ s^{-2}/C = \mathbf{1.86 \times 10^4\ V.}$

© 40.

Energy acquired $= 1000\ eV$
$= 1000 \times 1.602 \times 10^{-19}$
$= 1.602 \times 10^{-16}\ J$

$\frac{1}{2}mv^2 = 1.602 \times 10^{-16}\ J$

$\frac{1}{2} \times 9.1 \times 10^{-31} v^2 = 1.602 \times 10^{-16}\ J$

$v^2 = \frac{2 \times 1.602 \times 10^{-16}}{9.1 \times 10^{-31}} = 3.521 \times 10^{14}$

$v = 1.876 \times 10^7\ ms^{-1}$

Now, $\lambda = \frac{h}{mv}$

$= \frac{6.626 \times 10^{-34}\ kg\ m^2 s^{-1}}{(9.1 \times 10^{-31} kg) \times (1.876 \times 10^7\ ms^{-1})}$

$= \mathbf{3.88 \times 10^{-11}\ m}$

© 41. $\lambda = \frac{v}{\nu}$ or $\frac{v}{\nu} = \frac{h}{mv} \quad \therefore \quad \nu = \frac{mv^2}{h}$

$\frac{1}{2}mv^2 = 5.85 \times 10^{-25}$

$mv^2 = 2 \times 5.85 \times 10^{-25}$

$\therefore \quad \nu = \frac{2 \times 5.85 \times 10^{-25}}{6.63 \times 10^{-34}}$

$= \mathbf{1.76 \times 10^9\ s^{-1}}$

© 42. $\lambda = \frac{h}{mv}$

or $v = \frac{h}{m\lambda}$

$= \frac{6.63 \times 10^{-34}\ kg\ m^2 s^{-1}}{(9.1 \times 10^{-31} kg) \times (100 \times 10^{-10} m)}$

$= \mathbf{7.28 \times 10^4\ ms^{-1}}$

© 43. $\frac{1}{2}mv^2 = K.E.$

or $v^2 = \frac{2K.E.}{m}$

$= \frac{2 \times 1.375 \times 10^{-25}}{9.1 \times 10^{-31}}$

$= 0.3022 \times 10^6\ m^2 s^{-1}$

$\therefore \quad v = 5.5 \times 10^2\ ms^{-1}$

$\lambda = \frac{6.63 \times 10^{-34}}{9.1 \times 10^{-31} \times 5.5 \times 10^2}$

$= \mathbf{1.32 \times 10^{-6}\ m}$

© 44. $\Delta v = \frac{h}{4\pi m \Delta x} \quad \Delta x = 0.1\ Å \text{ or } = 0.1 \times 10^{-10}\ m$

$\Delta v = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 9.11 \times 10^{-31} \times 0.1 \times 10^{-10}}$

$= \mathbf{5.79 \times 10^6\ ms^{-1}}$

© 45. Uncertainty in the speed of ball

$= \frac{90 \times 4}{100} = \mathbf{3.6\ ms^{-1}}$

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Uncertainty in position, Δx

$$= \frac{h}{4\pi m \Delta v}$$

$$= \frac{6.626 \times 10^{-34}\,\text{Js}}{4 \times 3.14 \times 10 \times 10^{-3}\,\text{kg} \times 36\,\text{ms}^{-1}}$$

$$= \mathbf{1.46 \times 10^{-33}\ m}$$

Q 46. $\Delta v = \dfrac{1}{4\pi m \Delta x} = \dfrac{6.626 \times 10^{-34}}{4 \times 3.14 \times 1.1 \times 10^{-27} \times 3 \times 10^{-12}}$

$$= \mathbf{1.59 \times 10^{4}\ ms^{-1}.}$$

Q 47. $m = \dfrac{h}{4\pi \Delta x \,.\, \Delta v}$

$$= \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 10^{-10} \times 5.27 \times 10^{-24}}$$

$$= \mathbf{0.10\ kg}$$

Q 48. $\Delta v = \dfrac{1}{100} \times \dfrac{3.0 \times 10^{8}}{10} = \mathbf{3.0 \times 10^{5}}$

$$\Delta x = \frac{h}{4\pi\, m.\, \Delta v}$$

$$= \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 1.66 \times 10^{-27} \times 3.0 \times 10^{5}}$$

$$= \mathbf{1.06 \times 10^{-13}\ m}$$

Q 49. $\Delta v = \dfrac{3 \times 10^{7} \times 0.5}{100} = 1.5 \times 10^{5}\ \text{ms}^{-1}$

$$\Delta x = \frac{h}{4\pi m \Delta v}$$

$$= \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 1.66 \times 10^{-27} \times 1.5 \times 10^{5}}$$

$$= \mathbf{2.11 \times 10^{-13} m}$$

Chapter Summary

Key Terms & Laws

- **Electromagnetic spectrum** is the arrangement of different types of electromagnetic radiations in the increasing order of wavelengths (or decreasing frequencies).
- **Planck's quantum theory** states that radiant energy is not emitted continuously but discontinuously in the form of small packets of energy called **quantum** or **photon** (for light), each having energy = $h\nu$.
- **de Broglie principle**. All microscopic material particles in motion have dual character *i.e.*, particle and wave characteristics.

$$\lambda = \frac{h}{mv} \quad \text{or} \quad \frac{h}{p}$$

Dual nature of electrons was experimentally verified by Davisson and Germer (1927) and G. Thomson (1928).

- **Heisenberg uncertainty principle** states that it is impossible to measure simultaneously both the position and momentum (or velocity) with absolute accuracy for a microscopic particle. Mathematically, it may be expressed as:

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

- **Schrodinger wave equation** is a mathematical equation to describe behaviour of electron in an atom. Schrodinger wave equation may be expressed as :

$\hat{H}\psi = E\psi$, where ψ gives the amplitude of electron wave and ψ^2 is the probability density.

- **Electronic configuration** gives the distribution of electrons in various orbitals in an atom.
- **Quantum numbers.** A set of four numbers which give complete information about any electron in an atom.
- **Aufbau rule** states that the orbitals are filled in the order of increasing energy, starting with the orbital of lowest energy.
- **Pauli's exclusion principle.** No two electrons in an atom can have same set of all the four quantum numbers. This means that an orbital can accommodate only two electrons having opposite spins.
- **Hund's rule.** The pairing of electrons in orbitals of a same subshell cannot take place until all orbitals are singly occupied with parallel spin.

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QUICK CHAPTER ROUND UP

Energy of photon, $E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$

Einstein equation for photoelectron emission

$$\frac{1}{2}mv^2 = h\nu - h\nu_o$$

($h\nu_o$ ↓ work function)

ν_0 = threshold frequency

Rydberg equation

$$\frac{1}{\lambda} = \bar{\nu}(cm^{-1}) = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$n_2 > n_1$, R = 109677

Spectral lines of H-atom

Lyman	$n_1 = 1$,	$n_2 = 2, 3, 4, 5,$	⇒ ultraviolet
Balmer	$n_1 = 2$,	$n_2 = 3, 4, 5, 6,$	⇒ visible
Paschen	$n_1 = 3$,	$n_2 = 4, 5, 6$	⇒ Infrared
Brackett	$n_1 = 4$,	$n_2 = 5, 6, 7$	
Pfund	$n_1 = 5$,	$n_2 = 6, 7, 8$	

de-Broglie equation, $\lambda = \frac{h}{mv}$

Relationship between K.E. and λ of moving particle

$$\lambda = \frac{h}{\sqrt{2 \times K.E. \times m}}$$

Heisenberg uncertainly principle

$$\Delta x \times \Delta p \geq \frac{h}{4\pi};\ \Delta x \times \Delta v \geq \frac{h}{4\pi m}$$

Quantum Numbers

- **Principal quantum number** (n) tells about *the energy of the electron and size of the shell.*
- **Azimuthal quantum number** (l) tells about *the shape of the orbital (called subshell).*
- **Magnetic quantum number** (m) tells about the orientation of the electron cloud in a subshell.
- **Spin quantum number** (s) tell about the spin of the electron.

Name	Symbol	Information provided	Permitted values
Principal	n	shell	1, 2, 3, 4...
Azimuthal	l	subshell	0, 1, 2, 3 ... $(n-1)$
Magnetic	m_l	orbital	$-l$ ... 0 ... $+l$
Spin	m_s	spin	+½, – ½

For each orbital
No. of nodes = $n - l - 1$
No. of nodal planes = l

- $3d_{z^2}$ orbital has electron density in all the three axes.

Bohr model

- Bohr model gave the concept of well defined circular **orbits** or **energy levels** in which energy remains constant.
- **Angular momentum quantized,** $mvr = \frac{nh}{2\pi}$
- **Energy of electron in an orbit**

$$= -\frac{2\pi^2 m_e e^4 Z^2}{n^2 h^2} = -\frac{2.18 \times 10^{-18} Z^2}{n^2}\ J \text{ per atom}$$

$$= -\frac{1.312 \times 10^6 Z^2}{n^2}\ J \text{ per mol} = -\frac{13.6\ Z^2}{n^2}\ eV\ atom^{-1}$$

- **Bohr radius of an orbit**

$$r_n = \frac{0.059\ n^2}{Z}\ Å$$

e.g., For H atom, r_1 = 0.059 Å, r_2 = 2.12 Å
r_3 = 4.77 Å
For He^+, r_1 = 0.0295 Å, r_2 = 1.06 Å

$$r_n(\text{H-like}) = \frac{r_n(\text{H atom})}{Z}$$

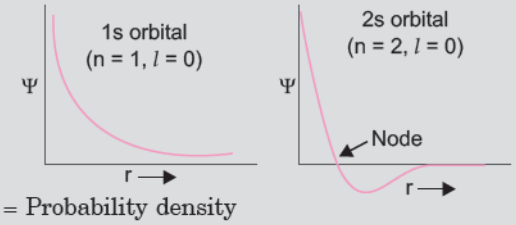
- **Velocity** $v = \frac{2.19 \times 10^6 Z}{n} = ms^{-1}$
- **No. of revolutions** $= \frac{2\pi m v Z e^2}{n^2 h^2}$

Schrodinger wave equation

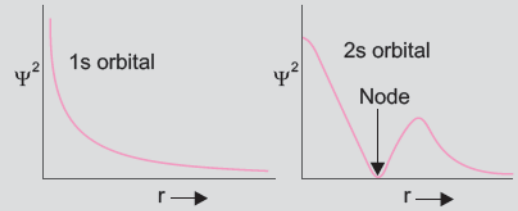
$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

or $\hat{H}\psi = E\psi$

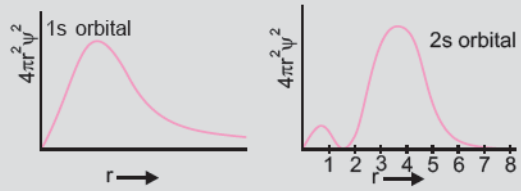
ψ = Radial wave function



ψ^2 = Probability density



$4\pi r^2\psi^2$ = Radial probability function



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Sequence of energy levels
- 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*.

- Cr $(3d^5 4s^1)$ and Cu $(3d^{10} 4s^1)$ have anomalous configurations because of extra stability associated with half filled and completely filled orbitals.

NCERT FILE Solved

NCERT Textbook Exercises

Q. 1. (*i*) Calculate the number of electrons which will together weigh one gram.

(*ii*) Calculate the mass and charge of one mole of electrons.

Ans. (*i*) Mass of one electron = 9.11×10^{-31} kg

$\therefore$ 9.11×10^{-31} kg = 1 electron

$$1 \text{ g or } 10^{-3} \text{ kg} = \frac{1}{9.11 \times 10^{-31}} \times 10^{-3} \text{ electrons}$$

$$= 1.098 \times 10^{27} \text{ electrons}$$

(*ii*) Mass of one electron = 9.11×10^{-31} kg

Mass of 1 mol of electrons = $9.11 \times 10^{-31} \times 6.022 \times 10^{23}$

$= 5.486 \times 10^{-7}$ kg.

Charge on one electron

$= 1.602 \times 10^{-19}$ C

Charge of 1 mol of electrons

$= 1.602 \times 10^{-19} \times 6.022 \times 10^{23}$ Coulombs

$= 9.647 \times 10^{4}$ C

Q. 2. (*i*) Calculate the total number of electrons present in one mole of methane.

(*ii*) Find (*a*) the total number and (*b*) the total mass of neutrons in 7 mg of ^{14}C. (Assume that mass of a neutron = 1.675×10^{-27} kg).

(*iii*) Find (*a*) the total number and (*b*) the total mass of protons in 34 mg of NH_3 at STP. Will the answer change if the temperature and pressure are changed ?

Ans. (*i*) 1 molecule of methane (CH_4) contains electrons = 6 + 4 = 10

1 mole or 6.022×10^{23} molecules of CH_4 will contain electrons = $6.022 \times 10^{23} \times 10$

$= 6.022 \times 10^{24}$

(*ii*) In ^{14}C

No. of neutrons + No. of Protons = 14

No. of protons = 6

$\therefore$ No. of neutrons + 6 = 14

$\therefore$ No. of neutrons = 14 – 6 = 8

Now 1 mol of ^{14}C = 14 g C

or $= 6.022 \times 10^{23}$ atoms of ^{14}C

$= 6.022 \times 10^{23} \times 8$ neutrons

$= 4.8176 \times 10^{24}$ neutrons

(*a*) 14 g of ^{14}C contain = 4.8176×10^{24} neutrons

7mg (7×10^{-3} g) of ^{14}C contain

$$= \frac{4.8176 \times 10^{24}}{14} \times 7 \times 10^{-3} \text{ neutrons}$$

$= 2.4088 \times 10^{21}$ neutrons

(*b*) Mass of 1 neutron = 1.675×10^{-27} kg

$\therefore$ Mass of 2.4088×10^{21} neutrons

$= 1.675 \times 10^{-27} \times 2.4088 \times 10^{21}$kg

$= 4.035 \times 10^{-6}$ kg.

(*iii*) 1 mole of NH_3 = 17g NH_3 = 6.022×10^{23} molecules of NH_3

1 molecule of NH_3 contains protons = 7 + 3 = 10

(*a*) 17g of NH_3 contain molecules = 6.022×10^{23}

34 mg of NH_3 contain molecules

$$= \frac{6.022 \times 10^{23}}{17} \times 34 \times 10^{-3}$$

$= 1.2044 \times 10^{21}$

No. of protons in 34 mg NH_3 = $1.204 \times 10^{21} \times 10$

$= 1.204 \times 10^{22}$

(*b*) Mass of proton = 1.6726×10^{-27}

$\therefore$ Mass of 1.204×10^{22} protons

$= 1.6726 \times 10^{-27} \times 1.204 \times 10^{22}$

$= 2.0138 \times 10^{-5}$ kg

There is no effect of temperature and pressure.

Q. 3. How many neutrons and protons are there in the following nuclei ?

$^{13}_{6}C$, $^{16}_{8}O$, $^{24}_{12}Mg$, $^{56}_{26}Fe$, $^{88}_{38}Sr$

Ans.

Nucleus	Z	A	*p*	*n* (A–Z)
$^{13}_{6}C$	6	13	6	13 – 6 = 7
$^{16}_{8}O$	8	16	8	16 – 8 = 8
$^{24}_{12}Mg$	12	24	12	24 – 12 = 12
$^{56}_{26}Fe$	26	56	26	56 – 26 = 30
$^{88}_{38}Sr$	38	88	38	88 – 38 = 50

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Q. 4. Write the complete symbol for the atom with the given atomic number (Z) and atomic mass (A)
(*i*) Z = 17, A = 35
(*ii*) Z = 92, A = 233
(*iii*) Z = 4, A = 9

Ans. (*i*) $^{35}_{17}Cl$ (*ii*) $^{233}_{92}U$ (*iii*) $^{9}_{4}Be$

Q. 5. Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate the frequency (ν) and wavenumber ($\bar{\nu}$) of the yellow light.

Ans. *Refer Solved Example 6 (Page 13).*

Q. 6. Find energy of each of the photons which :
(*i*) correspond to light of frequency 3×10^{15} Hz.
(*ii*) have wavelength of 0.50 Å

Ans. (*i*) $E = h\nu$

$= (6.626 \times 10^{-34}\ Js) \times (3 \times 10^{15}\ s^{-1})$

$= \mathbf{1.988 \times 10^{-18}\ J}$

(*ii*) $E = h\nu = \dfrac{hc}{\lambda}$

$= \dfrac{(6.626 \times 10^{-34}\ Js) \times (3 \times 10^{8}\ ms^{-1})}{(0.50 \times 10^{-10}\ m)}$

$= \mathbf{3.98 \times 10^{-15}\ s}$

Q. 7. Calculate the wavelength, frequency and wavenumber of a light wave whose period is 2.0×10^{-10}s.

Ans. (*i*) Frequency $= \dfrac{1}{\text{Period}} = \dfrac{1}{2.0 \times 10^{-10}\ s} = 5 \times 10^{9}\ s^{-1}$

(*ii*) Wavelength, $\lambda = \dfrac{c}{\nu} = \dfrac{3 \times 10^{8}\ ms^{-1}}{5 \times 10^{9}\ s^{-1}} = 6.0 \times 10^{-2}\ m$

(*iii*) Wave number $\bar{\nu} = \dfrac{1}{\lambda} = \dfrac{1}{6.0 \times 10^{-2}} = 16.66\ m^{-1}$

Q. 8. What is the number of photons of light with a wavelength of 4000 pm that provide 1J of energy ?

Ans. Wavelength of light, λ = 4000 pm

$= 4000 \times 10^{-12}\ m = 4 \times 10^{-9}\ m$

Energy of 1 photon,

$E = \dfrac{hc}{\lambda}$

$h = 6.626 \times 10^{-34}\ J\ s,\ c = 3.0 \times 10^{8}\ m\ s^{-1}$

$\therefore\quad E = \dfrac{6.626 \times 10^{-34} \times 3.0 \times 10^{8}}{4 \times 10^{-9}}$

$= 4.97 \times 10^{-17}\ J$

No. of photons providing 1 J of energy

$= \dfrac{1}{4.97 \times 10^{-17}} = \mathbf{2.01 \times 10^{16}}$

Q. 9. A photon of wavelength 4×10^{-7} m strikes on metal surface, the work function of the metal being 2.13 eV. Calculate (*i*) the energy of the photon (eV), (*ii*) the kinetic energy of the emission, and (*iii*) the velocity of the photoelectron (1 eV = 1.602×10^{-19}J)

Ans. (*i*)Energy of photon

$E = h\nu = \dfrac{hc}{\lambda}$

$\lambda = 4.0 \times 10^{-7}$m, $\quad c = 3.0 \times 10^{8}\ m\ s^{-1}$

$h = 6.626 \times 10^{-34}\ J\ s,$

$\therefore\ E = \dfrac{(6.626 \times 10^{-34}\ Js) \times (3.0 \times 10^{8}\ m)}{(4.0 \times 10^{-7}\ m)}$

$= 4.97 \times 10^{-19}\ J$

or $= \dfrac{4.97 \times 10^{-19}}{1.6020 \times 10^{-19}} = \mathbf{3.10\ eV.}$

(*ii*) Kinetic energy of emission

K.E. = hν − hν$_0$

hν = 3.10 eV and hν$_0$ (work function) = 2.13eV

∴ K.E. = 3.10 − 2.13 = 0.97 eV

(*iii*) Now, K.E. $= \dfrac{1}{2}\ mv^2$

or $\dfrac{1}{2} mv^2 = 0.97\ eV = 0.97 \times 1.602 \times 10^{-19}\ J$

or $\dfrac{1}{2} \times (9.11 \times 10^{-31}kg)\ v^2 = 0.97 \times 1.602 \times 10^{-19}\ J$

$v^2 = \dfrac{2 \times 0.97 \times 1.602 \times 10^{-19}\ kgm^2s^{-2}}{9.11 \times 10^{-31}kg}$

$= 34.12 \times 10^{10}\ m^2\ s^{-2}$

$\therefore\quad v = \mathbf{5.84 \times 10^{5}\ m\ s^{-1}}$

Q. 10. Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}.

Ans. Energy possessed by electromagnetic radiation with wavelength 242 nm will be equal to ionization energy,

$E = h\nu = \dfrac{hc}{\lambda}$

$h = 6.626 \times 10^{-34}\ J\ s$

$c = 3.0 \times 10^{8}\ m,\ \lambda = 242 \times 10^{-9}\ m$

$\therefore\quad E = \dfrac{(6.626 \times 10^{-34}\ J\ s) \times (3.0 \times 10^{8}\ m\ s^{-1})}{(242 \times 10^{-9}\ m)}$

$= 8.21 \times 10^{-19}\ J$

Ionization energy per mol = $8.21 \times 10^{-19}\ J \times 6.023 \times 10^{23}$

$= 494 \times 10^{3}\ J = \mathbf{494\ kJ\ mol^{-1}.}$

Q. 11. A 25 watt bulb emits monochromatic yellow light of wavelength of 0.57 μm. Calculate the rate of emission of quanta per second.

Ans. Energy of one photon,

$E = h\nu = \dfrac{hc}{\lambda}$

$h = 6.626 \times 10^{-34}\ J\ s$

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$c = 3.0 \times 10^8$ m, $\lambda = 0.57$ μm
$= 0.57 \times 10^{-6}$ m

$$E = \frac{6.63 \times 10^{-34} \times 3.0 \times 10^8}{0.57 \times 10^{-6}}$$

$= 3.487 \times 10^{-19}$ J

Now, 25 Watt = 25 J/s

$$\therefore \text{ No. of photons emitted per second } = \frac{25}{3.487 \times 10^{-19}}$$

$= \mathbf{7.17 \times 10^{19} s^{-1}}$.

Q. 12. Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 Å. Calculate threshold frequency (ν_0) and work function (W_0) of the metal.

Ans. K.E. $= h\nu - h\nu_0$

If the velocity is zero, K.E. = 0

$\therefore \quad 0 = h\nu - h\nu_0$

or $\quad h\nu = h\nu_0 \quad$ or $\quad \nu = \nu_0$

$$\therefore \quad \nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{6800 \times 10^{-10} \text{ m}}$$

$= 4.41 \times 10^{14}$ s^{-1}

Threshold frequency $= 4.41 \times 10^{14}$ s^{-1}

Work function $= h\nu_0 = 6.626 \times 10^{-34} \times 4.41 \times 10^{14}$

$= \mathbf{2.92 \times 10^{-19}}$ **J.**

Q. 13. What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with $n = 4$ to an energy level with $n = 2$?

Ans. *Refer Solved Example 17 (Page 21).*

Q. 14. How much energy is required to ionise a H-atom if the electron occupies $n = 5$ orbit ? Compare your answer with the ionization enthalpy of H-atom (energy required to remove the electron from $n = 1$ orbit).

Ans. $E_n = \dfrac{-21.8 \times 10^{-19}}{n^2}$ J atom^{-1}

For ionization from 5th orbit, $n_1 = 5$, $n_2 = \infty$

$$\Delta E = E_2 - E_1 = -21.8 \times 10^{-19} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$$= -21.8 \times 10^{-19} \left(\frac{1}{\infty} - \frac{1}{5^2}\right)$$

$$= -21.8 \times 10^{-19} \times \left(-\frac{1}{25}\right)$$

$= 8.72 \times 10^{-20}$ J

For ionization from Ist orbit, $n_1 = 1$, $n_2 = \infty$

$$\Delta E' = -21.8 \times 10^{-19} \left(\frac{1}{\infty} - \frac{1}{1^2}\right)$$

$= 21.8 \times 10^{-19}$ J

$$\frac{\Delta E'}{\Delta E} = \frac{21.8 \times 10^{-19} \text{ J}}{8.72 \times 10^{-20}}$$

$= \mathbf{25.}$

Thus, the energy required to remove electron from Ist orbit is 25 times than that required to remove electron from 5th orbit.

Q. 15. What is the maximum number of emission lines when the excited electron of a H-atom in $n = 6$ drops to the ground state ?

Ans. *Refer Solution to Practice Problems 25 (Page 70).*

Q. 16. (*i*) The energy associated with the first orbit in the hydrogen atom is -2.18×10^{-18} J atom^{-1}. What is the energy asociated with the fifth orbit ?
(*ii*) Calculate the radius of Bohr's fifth orbit for hydrogen atom.

Ans. *Refer Solved Example 22 (Page 28).*

Q. 17. Calculate the wavenumber for the longest wavelength transition in the Balmer series of atomic hydrogen.

Ans. $\bar{\nu} = R\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

For Balmer series $n_1 = 2$, for longest wavelength, $\bar{\nu}$ should be minimum so that $n_2 = 3$.

$$\bar{\nu} = (1.097 \times 10^7 \text{m}^{-1}) \left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$= 1.097 \times 10^7 \times \frac{5}{36}$$

$= \mathbf{1.523 \times 10^6 \text{ m}^{-1}}$.

Q. 18. What is the energy in joules, required to shift the electron of the hydrogen atom from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of the light emitted when the electron returns to the ground state ? The ground state electron energy is -2.18×10^{-11} ergs.

Ans. The gound state energy is -2.18×10^{-11} ergs.,

$$\therefore \quad E_n = -\frac{2.18 \times 10^{-11}}{n^2} \text{ ergs}$$

$$\Delta E = E_5 - E_1 = -2.18 \times 10^{-11} \left(\frac{1}{5^2} - \frac{1}{1^2}\right)$$

$$= 2.18 \times 10^{-11} \times \frac{24}{25} = 2.093 \times 10^{-11} \text{ ergs}$$

or $\quad = 2.093 \times 10^{-18}$ J (1 erg = 10^{-7}J)

When electron returns to ground state (*i.e.*, $n = 1$), energy emitted $= 2.093 \times 10^{-18}$ J

Now, $\Delta E = \dfrac{hc}{\lambda}$ or $\lambda = \dfrac{hc}{\Delta E}$

$$= \frac{(6.626 \times 10^{-34} \text{ Js}) \times (3.0 \times 10^8 \text{ ms}^{-1})}{(2.093 \times 10^{-18} \text{ J})}$$

$= 9.50 \times 10^{-8}$ m

or $\quad = \mathbf{950}$ **Å.**

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Q. 19. The electron energy in hydrogen atom is given by $E_n = (-2.18 \times 10^{-18})/n^2$ J. Calculate the energy required to remove an electron completely from the n = 2 orbit. What is the longest wavelength of light in cm that can be used to cause this transition?

Ans. $\Delta E = E_\infty - E_2$

$$= 0 - \left(-\frac{2.18\times10^{-18}\text{ J atom}^{-1}}{2^2}\right)$$

$$= 5.45 \times 10^{-19}\text{ J atom}^{-1}$$

$$\Delta E = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{\Delta E}$$

$$\therefore \quad \lambda = \frac{\left(6.626\times10^{-34}\text{ Js}\right)\times\left(3.0\times10^{8}\text{ ms}^{-1}\right)}{5.45\times10^{-19}\text{ J atom}^{-1}}$$

$$= 3.647 \times 10^{-7}\text{m}$$

or $= \mathbf{3.647 \times 10^{-5}\ cm.}$

Q. 20. Calculate the wavelength of an electron moving with a velocity of 2.05×10^7 ms^{-1}

Ans. *Refer Solved Example 31 (Page 38).*

Q. 21. The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wavelength.

Ans. *Refer Solved Example 39. (Page 39).*

Q. 22. Which of the following are isoelectronic species *i.e.*, those having the same number of electrons?

Na^+, K^+, Mg^{2+}, Ca^{2+}, S^{2-}, Ar.

Ans. Na^+, Mg^{2+}

K^+, Ca^{2+}, S^{2-} and Ar are isoelectronic.

Q. 23. (*i*) Write the electronic configurations of the following ions : (*a*) H^- (*b*) Na^+ (*c*) O^{2-} (*d*) F^-

(*ii*) What are the atomic numbers of elements whose outermost electrons are represented by (*a*) $3s^1$ (*b*) $2p^3$ and (*c*) $3p^5$?

(*iii*) Which atoms are indicated by the following configurations?

(*a*) [He] $2s^1$ (*b*) [Ne]$3s^2\,3p^3$ (*c*) $4s^2\,3d^1$

Ans. (*i*) *Refer Solved Example 57 (Page 63).*

(*ii*) (*a*) 11 (*b*) 7 (*c*) 17

(*iii*) (*a*) Li (*b*) P (*c*) Sc

Q. 24. What is the lowest value of *n* that allows *g* orbitals to exist?

Ans. $n = 5$

Q. 25. An electron is in one of the 3d orbitals. Give the possible values of *n*, *l* and m_l for this electron.

Ans. $n = 3$, $l = 2$ and for $l = 2$, $m_l = -2, -1, 0, +1, +2$.

Q. 26. An atom of an element contains 29 electrons and 35 neutrons. Deduce (*i*) the number of protons and (*ii*) the electronic configuration of the element.

Ans. (*i*) No. of protons = 29

(*ii*) Atomic number = 29

Electronic configuration : $[Ar]^{18}\,3d^{10}4s^1$.

Q. 27. Give the number of electrons in the species H_2^+, H_2 and O_2^+.

Ans. H_2^+ : 1 , H_2 = 2, O_2^+ = 15.

Q. 28. (*i*) An atomic orbital has *n* = 3. What are the possible values of *l* and m_l?

(*ii*) List the quantum numbers (m_l and *l*) of electrons for 3*d* orbital.

(*iii*) Which of the following orbitals are possible?

1*p*, 2*s*, 2*p* and 3*f*

Ans. (*i*) For $n = 3$, $l = 0, 1, 2$

When $l = 0$, $m_l = 0$

When $l = 1$, $m_l = -1, 0, +1$

When $l = 2$, $m_l = -2, -1, 0, +1, +2$

(*ii*) $n = 3$, $l = 2$ and for $l = 2$, $m_l = -2, -1, 0, +1, +2$

(*iii*) 2*s*, 2*p* are possible.

Q. 29. Using *s*, *p*, *d* notations, describe the orbital with the following quantum numbers.

(*a*) $n = 1$, $l = 0$; (*b*) $n = 3$; $l = 1$

(*c*) $n = 4$; $l = 2$; (*d*) $n = 4$; $l = 3$

Ans. *Refer solved Example 49 (Page 49).*

Q. 30. Explain, giving reasons, which of the following sets of quantum numbers are not possible.

(*a*)	$n = 0$,	$l = 0$,	$m_l = 0$,	$m_s = +1/2$
(*b*)	$n = 1$,	$l = 0$,	$m_l = 0$,	$m_s = -1/2$
(*c*)	$n = 2$,	$l = 1$,	$m_l = 0$,	$m_s = +1/2$
(*d*)	$n = 2$,	$l = 1$,	$m_l = 0$,	$m_s = -1/2$
(*e*)	$n = 3$,	$l = 3$,	$m_l = -3$,	$m_s = +1/2$
(*f*)	$n = 3$,	$l = 1$,	$m_l = 0$,	$m_s = +1/2$

Ans. *Refer Solved Example 51 (Page 49).*

Q. 31. How many electrons in an atom may have the following quantum numbers?

(*a*) $n = 4$, $m_s = -1/2$ (*b*) $n = 3$, $l = 0$

Ans. (*i*) Total number of electrons in $n = 4$ are $2 \times 4^2 = 32$

Half of these *i.e.*, 16 electrons have $m_s = -1/2$

(*ii*) It means 3*s* orbital. It can have 2 electrons.

Q. 32. Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de-Broglie wavelength associated with the electron revolving around the orbit.

Ans. According to Bohr's postulation of angular momentum

$$mvr = \frac{nh}{2\pi} \quad \text{or} \quad 2\pi r = n\frac{h}{mv} \qquad \ldots.(i)$$

According to de Broglie equation, $\lambda = \frac{h}{mv}$ .....(*ii*)

From (*i*) and (*ii*) we get

$$2\pi r = n\lambda$$

Thus, the circumference ($2\pi r$) of Bohr orbit for H-atom is an integral multiple of de Broglie wavelength.

For detail, *Refer Text (Page 35–37).*

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Q. 33. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum ?

Ans. For He^+ spectrum,

$$\frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Now, $n_1 = 2, n_2 = 4$ and $Z = 2$

$$\frac{1}{\lambda} = R \times (2)^2\left[\frac{1}{2^2} - \frac{1}{4^2}\right] = \frac{3}{4}R \quad ...(i)$$

For H atom $$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad ...(ii)$$

Since λ is the same, equating equations (i) and (ii)

$$\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$

Now, if $n_1 = 1$ and $n_2 = 2$.

Therefore, the transition from $n = 2$ to $n = 1$ in H atom will have the same wavelength as the transition from $n = 4$ to $n = 2$ in He^+.

Q. 34. Calculate the energy required for the process

$$He^+(g) \longrightarrow He^{2+}(g) + e^-$$

The ionization energy for the H atom in the ground state is 2.18×10^{-18} J atom $^{-1}$.

Ans. For H like species, $E_n = \frac{-2\pi^2 m Z^2 e^4}{n^2 h^2}$

For H atom, $IE = E_n - E_1$

$$= 0 - \left(-\frac{2\pi^2 m e^4}{1 \times h^2}\right)$$

$$= \frac{2\pi^2 m e^4}{h^2} = 2.18 \times 10^{-18} \text{ J atom}^{-1} \text{ (given)}$$

For the given process,

Energy required $= E_n - E_1$

$$= 0 - \left(-\frac{2\pi^2 m e^4 (2)^2}{(1^2 \times h^2)}\right) = 4 \times \frac{2\pi^2 m e^4}{h^2}$$

$$= 4 \times 2.18 \times 10^{-18} \text{ J}$$

$$= \mathbf{8.72 \times 10^{-18} J.}$$

Q. 35. If the diameter of a carbon atom is 0.15 nm, calculate the number of carbon atoms which can be placed side by side in a straight line across length of scale of length 20 cm long.

Ans. A carbon atom covers length = diameter of atom = 0.15 nm

$$= 0.15 \times 10^{-9} \times 10^2 \text{ cm}$$

$\therefore$ No. of carbon atoms which can be placed on 20 cm length

$$= \frac{20}{0.15 \times 10^{-9} \times 10^2} = 1.33 \times 10^9$$

Q. 36. 2×10^8 atoms of carbon are arranged side by side. Calculate the radius of carbon atom if the length of this arrangement is 2.4 cm.

Ans. An atom will cover length equal to its diameter

$$\text{Diameter of carbon atom} = \frac{2.4}{2 \times 10^8}$$

$$= 1.2 \times 10^{-8} \text{ cm}$$

$$= 1.2 \times 10^{-10} \text{ m}$$

$$\text{Radius of carbon atom} = \frac{1.2 \times 10^{-10}}{2}$$

$$= 0.6 \times 10^{-10} \text{ m}$$

$$= 0.06 \times 10^{-9} \text{ m}$$

$$= \mathbf{0.06 \text{ nm}}$$

Q. 37. The diameter of zinc atom is 2.6 Å. Calculate (a) radius of zinc atom in pm and (b) number of atoms present in a length of 1.6 cm if the zinc atoms are arranged side by side lengthwise.

Ans. (i) Diameter of zinc atom = 2.6 Å = 2.6×10^{-10}m

$$\text{Radius} = \frac{2.6 \times 10^{-10}}{2}$$

$= 1.3 \times 10^{-10}\text{m} = 130 \times 10^{-12}\text{m}$

or $= 130$ pm

(ii) No. of Zn atoms present on a 1.6 cm length $= \frac{1.6}{2.6 \times 10^{-10} \times 10^2} = 6.154 \times 10^7$

Q. 38. A certain particle carries 2.5×10^{-16}C of static electric charge. Calculate the number of electrons present in it.

Ans. Charge of one electron = 1.602×10^{-19} C

$$\text{No. of electrons present} = \frac{2.5 \times 10^{-16}}{1.602 \times 10^{-19}} = 1.56 \times 10^3$$

Q. 39. In Millikan's experiment, static electric charge on the oil drops has been obtained by shining X-rays. If the static electric charge on the oil drop is -1.282×10^{-18}C, calculate the number of electrons present in it.

Ans. $$\text{Number of electrons} = \frac{-1.282 \times 10^{-18}\text{C}}{-1.6022 \times 10^{-19}\text{C}} = 8$$

Q. 40. In Rutherford's experiment, generally the thin foil of heavy atoms, like gold, platinum, etc. have been used to be bombarded by the α-particles. If the thin foil of light atoms like aluminium, etc. is used, what difference would be observed from the above results ?

Ans. In Rutherford's experiment, heavy atoms have heavy nucleus carrying a large amount of positive charge. Therefore, some α-particles even got deflected back after hitting the nucleus. Because of large positive charge on the heavy nucleus, some α-particles are deflected through small angles which passed closer to the nucleus because of repulsion. However, if lighter atoms are used, their nuclei will be light and they will have small positive charge on the nucleus. As a result, the number of particles deflected back and those deflected through small angles will be very very small, almost negligible.

Q. 41. Symbols $^{79}_{35}Br$ and ^{79}Br can be written, whereas symbols $^{35}_{79}Br$ and ^{35}Br are not acceptable. Answer briefly.

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Ans. Atomic number of an element (say Br) is fixed but its mass number is not fixed depending upon the isotope. Hence, it is necessary to indicate mass number.

Q. 42. An element with mass number 81 contains 31.7% more neutrons as compared to protons. Assign the atomic symbol.

Ans. *Refer Solved Example 4 (Page 10).*

Q. 43. An ion with mass number 37 possesses one unit of negative charge. If the ion contains 11.1% more neutrons than the electrons, find the symbol of the ion

Ans. *Solutions to Practice Problem 8 (Page 69).*

Q. 44. An ion with mass number 56 contains 3 units of positive charge and 30.4% more neutrons than electrons. Assign the symbol to this ion.

Ans. *Refer Solved Example 5 (Page 10).*

Q. 45. Arrange the following type of radiations in increasing order of frequency : (*a*) radiation from microwave oven (*b*) amber light from traffic signal (*c*) radiation from FM radio (*d*) cosmic rays from outer space and (*e*) X-rays.

Ans. Cosmic rays < X-rays < amber light < microwave < FM.

Q. 46. Nitrogen laser produces a radiation at a wavelength of 337.1 nm. If the number of photons emitted is 5.6×10^{24}, calculate the power of this laser.

Ans. $E = N h\nu = \dfrac{Nhc}{\lambda}$

$$= \frac{\left(5.6\times10^{24}\right)\times\left(6.62\times10^{-34}\,\text{Js}\right)\times\left(3.0\times10^{8}\,\text{ms}^{-1}\right)}{337.1\times10^{-9}\,\text{m}}$$

$= \mathbf{3.3 \times 10^6\ J.}$

Q. 47. Neon gas is generally used in the sign boards. If it emits strongly at 616 nm, calculate (a) the frequency of emission, (b) distance travelled by this radiation in 30 s (c) energy of quantum and (d) number of quanta present if it produces 2 J of energy.

Ans. Wavelength of light, $\lambda = 616\ \text{nm} = 616 \times 10^{-9}\ \text{m}$

(*a*) Frequency $= \dfrac{c}{\lambda} = \dfrac{3.0\times10^{8}\,\text{ms}^{-1}}{616\times10^{-9}\,\text{m}}$

$= 4.87 \times 10^{14}\,\text{s}^{-1}$

(*b*) Distance traveled in 30 s

$= 30 \times 616 \times 10^{-9} \times 4.87 \times 10^{14}$

$= 9.0 \times 10^{9}\,\text{m}$

(*c*) Energy of quanta, $E = h\nu$

$= 6.626 \times 10^{-34}\,\text{Js} \times 4.87 \times 10^{14}\,\text{s}^{-1}$

$= 3.227 \times 10^{-19}\,\text{J}$

(*d*) No. of quanta in 2J of energy $= \dfrac{2}{3.227\times10^{-19}}$

$= 6.2 \times 10^{18}$ photons.

Q. 48. In astronomical observations, signals observed from the distant stars are generally weak. If the photon detector receives a total of 3.15×10^{-18} J from the radiations of 600 nm, calculate the number of photons received by the detector.

Ans. Energy of 1 photon,

$$E = \frac{hc}{\lambda}$$

$h = 6.626 \times 10^{-34}\,\text{Js}$, $c = 3.0 \times 10^{8}\,\text{ms}^{-1}$,

$\lambda = 600\,\text{nm} = 600 \times 10^{-9}\,\text{m}$

$$E = \frac{6.626\times10^{-34}\times3.0\times10^{8}}{600\times10^{-9}\,\text{m}}$$

$$= 3.31 \times 10^{-19}\,\text{J}$$

Total energy received $= 3.15 \times 10^{-18}$ J

No. of photons $= \dfrac{3.15\times10^{-18}}{3.31\times10^{-19}} = 9.52 \simeq 10$

Q. 49. Lifetimes of the molecules in the excited states are often measured by using pulsed radiation source of duration nearly in the nano second range. If the radiation source has the duration of 2 ns and the number of photons emitted during the pulse source is 2.5×10^{15}, calculate the energy of the source.

Ans. Frequency $= \dfrac{1}{2\times10^{-9}} = 0.5 \times 10^{9}\,\text{s}^{-1}$

Energy $= Nh\nu = (2.5 \times 10^{15}) \times (6.62 \times 10^{-34}\,\text{Js})$

$\times (0.5 \times 10^{9}\,\text{s}^{-1}) = 8.275 \times 10^{-10}\,\text{J}.$

Q. 50. The longest wavelength doublet absorption transition is observed at 589 and 589.6 nm. Calculate the frequency of each transition and energy difference between two excited states.

Ans. $\lambda_1 = 589\ \text{nm} = 589 \times 10^{-9}\,\text{m}$

$$\nu_1 = \frac{c}{\lambda_1} = \frac{3.0\times10^{8}\,\text{ms}^{-1}}{589\times10^{-9}\,\text{m}} = 5.093 \times 10^{14}\,\text{s}^{-1}$$

$\lambda_2 = 589.6\ \text{nm} = 589.6 \times 10^{-9}\,\text{m}$

$$\nu_2 = \frac{c}{\lambda_2} = \frac{3.0\times10^{8}\,\text{ms}^{-1}}{589.6\times10^{-9}\,\text{m}} = 5.088 \times 10^{14}\,\text{s}^{-1}$$

$\Delta E = h(\nu_2 - \nu_1)$

$= (6.626 \times 10^{-34}\,\text{Js})\,(5.093 - 5.088) \times 10^{14}\,\text{s}^{-1}$

$= \mathbf{3.44 \times 10^{-22}\ J}$

Q. 51. The work function for caesium atom is 1.9 eV. Calculate (*a*) the threshold wavelength and (*b*) the threshold frequency of the radiation. If the caesium element is irradiated with a wavelength 500 nm, calculate the kinetic energy and the velocity of the ejected photoelectron.

Ans. Work function,

$h\nu_0 = 1.9\ \text{eV} = 1.9 \times 1.602 \times 10^{-19}\,\text{J}$

$= 3.04 \times 10^{-19}\,\text{J}$

$\therefore$ Threshold frequency $= \dfrac{3.04\times10^{-19}\,\text{J}}{6.626\times10^{-34}\,\text{Js}}$

$= 4.59 \times 10^{14}\,\text{s}^{-1}$

Threshold wavelength, $\lambda_0 = \dfrac{c}{\nu_0}$

$$= \frac{3.0\times10^{8}\,\text{ms}^{-1}}{4.59\times10^{14}\,\text{s}^{-1}}$$

$= 6.54 \times 10^{-7}\,\text{m}$ or **654 nm**

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Now, energy of radiated light, $E = \frac{hc}{\lambda}$

$= \frac{6.626\times10^{-34}\times3.0\times10^{8}}{500\times10^{-9}} = 3.98\times10^{-19}\ J$

$\therefore$ K.E. of ejected electron $= 3.98\times10^{-19} - 3.04\times10^{-19}$
$= 9.4\times10^{-20}\ J$

$K.E. = \frac{1}{2}mv^2 = 9.4\times10^{-20}\ J$

$v^2 = \frac{9.4\times10^{-20}\times2}{9.1\times10^{-31}} = 20.66\times10^{10}$

$\therefore \quad v = (20.66\times10^{10})^{1/2} = 4.54\times10^{5}\ m\ s^{-1}$

Q. 52. Following results are observed when sodium metal is irradiated with different wavelengths. Calculate (a) threshold wavelength and, (b) Planck's constant.

λ(nm)	**500**	**450**	**400**
$v\times10^{-5}$ (cm s^{-1})	**2.55**	**4.35**	**5.35**

Ans. Let threshold wavelength be λ_0 nm = $\lambda\times10^{-9}$ m

$h(\nu-\nu_0) = \frac{1}{2}mv^2$

$h\left(\frac{c}{\lambda}-\frac{c}{\lambda_0}\right) = \frac{1}{2}mv^2$

or $hc\left(\frac{1}{\lambda}-\frac{1}{\lambda_0}\right) = \frac{1}{2}mv^2$

$hc\left(\frac{1}{500\times10^{-9}}-\frac{1}{\lambda_0\times10^{-9}}\right) = \frac{1}{2}mv^2$

$\frac{hc}{10^{-9}}\left(\frac{1}{500}-\frac{1}{\lambda_0}\right) = \frac{1}{2}\ m\ (2.55\times10^{5})^2 \quad ....(i)$

Similarly,

$\frac{hc}{10^{-9}}\left(\frac{1}{450}-\frac{1}{\lambda_0}\right) = \frac{1}{2}\ m\ (4.35\times10^{5})^2 \quad ....(ii)$

$\frac{hc}{10^{-9}}\left(\frac{1}{400}-\frac{1}{\lambda_0}\right) = \frac{1}{2}\ m\ (5.20\times10^{5})^2 \quad ....(iii)$

Dividing eq. (*ii*) by (*i*)

$\frac{\lambda_0-450}{450\lambda_0}\times\frac{500\lambda_0}{\lambda_0-500} = \left(\frac{4.35}{2.55}\right)^2$

$\frac{\lambda_0-450}{\lambda_0-500} = \frac{450}{500}\times\left(\frac{4.35}{2.55}\right)^2$

$\frac{\lambda_0-450}{\lambda_0-500} = 2.91$

or $\lambda_0 - 450 = 2.91\ \lambda_0 - 1455$

$1.91\ \lambda_0 = 1005$

$\therefore \quad \lambda_0 = 526.2$ nm or $= 526$ nm

Substituting the value of λ_0 in eqn. (*iii*), we get

$\frac{h\times(3.0\times10^{8})}{10^{-9}}\left(\frac{1}{400}-\frac{1}{526}\right) = \frac{1}{2}\times9.11\times10^{-31}\times(5.20\times10^{5})^2$

$\frac{h\times(3.0\times10^{8})}{10^{-9}}\left(\frac{526-400}{400\times526}\right) = 123.17\times10^{-21}$

$h = \frac{123.17\times10^{-21}\times10^{-9}\times400\times526}{3.0\times10^{8}\times126}$

$= \mathbf{6.84\times10^{-34}\ Js.}$

Q. 53. The ejection of the photoelectron from the silver metal in the photoelectric effect experiment can be stopped by applying the voltage of 0.35 V when the radiation 256.7 nm is used. Calculate the work function for silver metal.

Ans. Energy of incident radiation
= Work function + K.E. of photoelectrons
Energy of incident radiation,

$E = h\nu = \frac{hc}{\lambda}$

$= \frac{(6.626\times10^{-34}\ Js)\times(3.0\times10^{8}\ ms^{-1})}{(256.7\times10^{-9}\ m)}$

$= 7.74\times10^{-19}\ J$

or $= \frac{7.74\times10^{-19}\ J}{1.602\times10^{-19}} = 4.83$ eV

The potential energy gives the kinetic energy to the electrons.
Hence K.E. of the electron = 0.35 eV
Work function = 4.83 eV – 0.35 eV = **4.48 eV**

Q. 54. If the photon of the wavelength 150 pm strikes an atom and one of its inner bound electrons is ejected out with a velocity of 1.5×10^{7} m s^{-1}, calculate the energy with which it is bound to the nucleus.

Ans. Energy of incident photon

$= \frac{hc}{\lambda}$

$= \frac{(6.626\times10^{-34}\ Js)\times(3.0\times10^{8}\ ms^{-1})}{(150\times10^{-12}\ m)}$

$= 1.325\times10^{-15}\ J$

Energy of ejected electron

$= \frac{1}{2}mv^2$

$= \frac{1}{2}\times(9.11\times10^{-31}\ kg)\times(1.5\times10^{7}\ ms^{-1})^2$

$= 1.025\times10^{-16} J$

Energy with which the electron was bound to the nucleus

$= 13.25\times10^{-16} - 1.025\times10^{-16}$
$= 12.225\times10^{-16}\ J$

or $= \frac{12.225\times10^{-16}}{1.602\times10^{-19}} = \mathbf{7.63\times10^{3}\ eV.}$

Q. 55. Emission transitions in the Paschen series end at orbit $n = 3$ and start from orbit n and can be represented as $\nu = 3.29\times10^{15}$ (Hz) $[1/3^2 - 1/n^2]$ Calculate the value of n if the transition is observed at 1285 nm. Find the region of the spectrum.

Ans. $\nu = 3.29\times10^{15}\left(\frac{1}{3^2}-\frac{1}{n^2}\right)\ s^{-1}$

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$$\lambda = 1285 \text{ nm}$$

$$\therefore \quad \nu = \frac{c}{\lambda} = \frac{3.0\times10^{8}\,\text{ms}^{-1}}{1285\times10^{-9}\,\text{m}}$$

$$= 2.33 \times 10^{14}\,\text{s}^{-1}$$

$$2.33 \times 10^{14} = 3.29 \times 10^{15}\left(\frac{1}{9}-\frac{1}{n^2}\right)$$

$$\text{or} \quad \frac{1}{9}-\frac{1}{n^2} = \frac{2.33\times10^{14}}{3.29\times10^{15}} = 0.0708$$

$$-\frac{1}{n^2} = 0.0708 - \frac{1}{9} = -0.0403$$

$$\frac{1}{n^2} = 0.0403$$

$$\text{or} \quad n^2 = 24.82$$

$$\therefore \quad n = 5$$

Transition is obtained in infrared region.

Q. 56. Calculate the wavelength for the emission transition if it starts from the orbit having radius 1.3225 nm and ends at 211.6 pm. Name the series to which this transition belongs and the region of the spectrum.

Ans. Radius of nth orbit of H like species $= \frac{0.529\,n^2}{Z}$ Å

$$\text{or} \quad = \frac{52.9n^2}{Z} \text{ pm}$$

$$r_1 = 1.3225 \text{ nm} = 1322.5 \text{ pm} = \frac{52.9n_1^2}{Z}$$

$$r_2 = 211.6 \text{ pm} = \frac{52.9\,n_2^2}{Z}$$

$$\therefore \quad \frac{r_1}{r_2} = \frac{1322.5}{211.6} = \frac{n_1^2}{n_2^2}$$

$$\therefore \quad \frac{n_1^2}{n_2^2} = 6.25 \text{ or } \frac{n_1}{n_2} = 2.5$$

If $n_2 = 2$, $n_1 = 5$, This transition corresponds to transition from 5th orbit to 2nd orbit. Hence, it belongs to Balmer series.

$$\text{Now, } \bar{\nu} = 1.097 \times 10^{7}\,\text{m}^{-1}\left(\frac{1}{2^2}-\frac{1}{5^2}\right)$$

$$= 1.097 \times 10^{7} \times \frac{21}{100}\,\text{m}^{-1}$$

$$\therefore \quad \lambda = \frac{1}{\bar{\nu}} = \frac{1}{23.037\times10^{5}\,\text{m}^{-1}}$$

$$= 434 \times 10^{-9}\text{m or } 434 \text{ nm}$$

It lies in the **visible region.**

Q. 57. Dual behaviour of matter proposed by de Broglie led to the discovery of electron microscope often used for the highly magnified images of biological molecules and other type of material. If the velocity of the electron in this microscope is 1.6×10^{6} ms^{-1}, calculate de Broglie wavelength associated with this electron.

Ans. $\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\,kg\,\text{m}^2\text{s}^{-1}}{\left(9.11\times10^{-31}\,kg\right)\times\left(1.6\times10^{6}\,\text{ms}^{-1}\right)}$

$$= 4.55 \times 10^{-10}\text{m}$$

or $= \mathbf{455\ pm.}$

Q. 58. Similar to electron diffraction, neutron diffraction microscope is also used for the determination of the structure of molecules. If the wavelength used here is 800 pm calculate the characteristic velocity associated with the neutron.

Ans. $\lambda = \frac{h}{mv}$ = or $\nu = \frac{h}{m\lambda}$

$$= \frac{6.626\times10^{-34}\,kg\,\text{m}^2\text{s}^{-1}}{1.675\times10^{-27}\,kg\ \times800\times10^{-12}\text{m}}$$

$$= \mathbf{4.94 \times 10^{2}\ ms^{-1}}$$

Q. 59. If the velocity of the electron in Bohr's first orbit is 2.19×10^{6} ms^{-1}, calculate the de Broglie wavelength associated with it.

Ans. *Refer Solved Example 35 (Page 38).*

Q. 60. The velocity associated with a proton moving in a potential difference of 1000 V is 4.37×10^{5} ms^{-1}. If the hockey ball of mass 0.1 kg is moving with this velocity, calculate the wavelength associated with this velocity.

Ans. $\lambda = \frac{h}{mv}$

$$= \frac{6.626\times10^{-34}\,kg\,\text{m}^2\text{s}^{-1}}{\left(0.1\,kg\right)\times\left(4.37\times10^{5}\,\text{ms}^{-1}\right)}$$

$$= 1.516 \times 10^{-28}\,\text{m}$$

Q. 61. If the position of the electron is measured within an accuracy of ± 0.002 nm, calculate the uncertainty in the momentum of the electron. Suppose the momentum of the electron is $\frac{h}{4\pi m} \times 0.05$ nm, is there any problem in defining this value.

Ans. *Refer Solved Example 46 (Page 43).*

Q. 62. The quantum numbers of six electrons are given below. Arrange them in order of increasing energies. If any of these combination(s) has/have the same energy lists :

(a) $n = 4$, $l = 2$, $m_l = -2$, $m_s = -1/2$
(b) $n = 3$, $l = 2$, $m_l = 1$, $m_s = +1/2$
(c) $n = 2$, $l = 0$, $m_l = 0$, $m_s = +1/2$
(d) $n = 2$, $l = 0$, $m_l = 0$, $m_s = -1/2$
(e) $n = 3$, $l = 3$, $m_l = 0$, $m_s = +1/2$
(f) $n = 3$, $l = 1$, $m_l = 0$, $m_s = +1/2$

Ans. *Refer Solved Example 58 (Page 64).*

Q. 63. The bromine atom possesses 35 electrons. It contains 6 electrons in 2*p* orbital, 6 electrons in 3*p* orbital and 5 electron in 4*p* orbital. Which of these electron experiences the lowest effective nuclear charge ?

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Ans. 4*p* electrons are farthest from the nucleus and therefore, these electrons will experience the lowest effective nuclear charge.

Q. 64. Among the following pairs of orbitals which orbital will experience the larger effective nuclear charge ? (*i*) 2*s* and 3*s*, (*ii*) 4*d* and 4*f*, (*iii*) 3*d* and 3*p*.

Ans. (*i*) 2*s* (*ii*) 4*d* (*iii*) 3*p*.

Q. 65. The unpaired electrons in Al and Si are present in 3*p* orbital. Which electrons will experience more effective nuclear charge from the nucleus ?

Ans. Unpaired electron in case of silicon will experience more effective nuclear charge.

Q. 66. Indicate the number of unpaired electrons in: (*a*) P, (*b*) Si, (*c*) Cr, (*d*) Fe and (*e*) Kr.

Ans. *Refer Solved Example 59 (Page 64).*

Q. 67. (*a*) How many sub-shells are associated with *n* = 4 ? (*b*) How many electrons will be present in the sub-shell having m_s value of –1/2 for *n* = 4 ?

Ans. Sub-shells in *n* = 4 are 4 *i.e.*, 4*s*, 4*p*, 4*d* and 4*f*

No. of electrons having $m_s = -1/2$ for *n* = 4 will be 16.

NCERT Exemplar Problems

Subjective Questions

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 109*

Short Answer Questions *Carrying 2 or 3 marks*

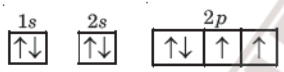
Q.1. Arrange *s*, *p* and *d* sub-shells of a shell in the increasing order of effective nuclear charge (Z_{eff}) experienced by the electron present in them.

Ans. *s*-orbitals shield the electrons from the nucleus more effectively than *p*-orbitals which in turn shield more effectively than *d*-orbitals. Hence, the subshells in the increasing order of effective nuclear charge is :

$$d < p < s$$

Q.2. Show the distribution of electrons in oxygen atom (atomic number 8) using orbital diagram.

Ans. O (Z = 8) :



Q.3. Nickel atom can lose two electrons to form Ni^{2+} ion. The atomic number of nickel is 28. From which orbital will nickel lose two electrons.

Ans. *Refer Conceptual Qs.* 2 Q.36 *(Page 67).*

Q.4. Which of the following orbitals are degenerate ?

$3d_{xy}$, $4d_{xy}$, $3d_{z^2}$, $3d_{yz}$, $4d_{yz}$, $4d_{z^2}$

Ans. *Refer Conceptual Qs.* 2 Q.37 *(Page 67).*

Q.5. Calculate the total number of angular nodes and radial nodes present in 3*p* orbital.

Ans. *Refer Conceptual Qs.* 2 Q.38 *(Page 67).*

Q.6. The arrangement of orbitals on the basis of energy is based upon their (*n* + *l*) value. Lower the value of (*n* + *l*), lower is the energy. For orbitals having same values of (*n* + *l*), the orbital with lower value of *n* will have lower energy.

I. Based upon the above information, arrange the following orbitals in the increasing order of energy.

(a) 1*s*, 2*s*, 3*s*, 2*p* **(b) 4*s*, 3*s*, 3*p*, 4*d***

(c) 5*p*, 4*d*, 5*d*, 4*f*, 6*s* **(d) 5*f*, 6*d*, 7*s*, 7*p***

II. Based upon the above information, solve the questions given below :

(a) Which of the following orbtials has the lowest energy ?

4*d*, 4*f*, 5*s*, 5*p*

(b) Which of the following orbitals has the highest energy ?

5*p*, 5*d*, 5*f*, 6*s*, 6*p*

Ans. *Refer Conceptual Qs.* 2 Q.39 *(Page 67).*

Q. 7. Which of the following will not show deflection from the path on passing through an electric field ?

Proton, cathode rays, electron, neutron.

Ans. Neutron is a neutral particle. Hence, it will not show deflection from the path on passing through an electric field.

Q. 8. An atom having atomic mass number 13 has 7 neutrons. What is the atomic number of the atom ?

Ans. Atomic mass, A = 13, *n* = 7

$n + p = 13$ $\quad \therefore p = 13 - 7 = 6$

Hence, atomic number, Z = *p* = 6

Q. 9. Wavelengths of different radiations are given below :

λ(A) = 300 nm **λ(B) = 300 μm**

λ(C) = 3 nm **λ(D) = 30 Å**

Arrange these radiations in the increasing order of their energies.

Ans. $E = h\nu$ or $= \frac{hc}{\lambda}$ or $E \propto \frac{1}{\lambda}$

$\lambda(A) = 300 \text{ nm} = 300 \times 10^{-9} \text{ m}$ or $= 3 \times 10^{-7} \text{ m}$;

$\lambda(B) = 300 \times 10^{-6} \text{ m} = 3 \times 10^{-4} \text{ m}$

$\lambda(C) = 3 \times 10^{-9} \text{ m}$, $\quad \lambda(D) = 30 \times 10^{-10} \text{ m} = 3 \times 10^{-9} \text{ m}$

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$\therefore$ Increasing order of energies is :

$$B < A < C = D$$

Q. 10. The electronic configuration of valence shell of Cu is $3d^{10}4s^1$ and not $3d^94s^2$. How is this configuration explained ?

Ans. This is because completely filled and half filled orbitals have extra stability. In $3d^{10}4s^1$, *d*-orbitals are completely filled and hence this configuration is more stable.

Q. 11. The Blamer series in the hydrogen spectrum corresponds to the transition from $n_1 = 2$, to $n_2 = 3, 4, ...$, This series lies in the visible region. Calculate the wave number of line associated with the transition in Balmer series when the electron moves to $n = 4$ orbit.
($R_H = 109677\ cm^{-1}$)

Ans.
$$\bar{\nu} = 109677\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) cm^{-1}$$

$$= 109677\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = 109677\left(\frac{1}{4} - \frac{1}{16}\right)$$

$$= 109677 \times \frac{3}{16} = 20564.4\ cm^{-1}$$

Q.12. According to de Broglie, matter should exhibit dual behaviour, that is both particle and wave like properties. However, a cricket ball of mass 100 g does not move like a wave when it is thrown by a bowler at a speed of 100 km/h. Calculate the wavelength of the ball and explain why it does not show wave nature.

Ans. $m = 100\ g = 0.1\ kg$

$$v = 100\ km/h = \frac{100 \times 1000}{60 \times 60}$$

$$= \frac{1000}{36} ms^{-1}$$

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} kg\ m^2 s^{-1}}{(0.1\ kg)\ (1000/36\ ms^{-1})}$$

$$= 2.387 \times 10^{-34} m$$

Since the wavelength is very small, the wave nature cannot be detected.

Q.13. What is the experimental evidence in support of idea that electronic energies in an atom are quantized ?

Ans. In the line spectrum of any element, lines of definite wavelength are obtained. These lines correspond to electronic transitions between fixed energy levels. Thus, the electrons in these energy levels have definite energy i.e, quantized values.

Q.14. Out of electron and proton which one will have, a higher velocity to produce matter waves of the same wavelength ? Explain it.

Ans. $\lambda = \frac{h}{mv}$. For the same value of λ, the electron will have higher velocity because it is lighter particle.

Q.15. A hypothetical electromagnetic wave is shown in Fig. 1. Find out the wavelength of the radiation.

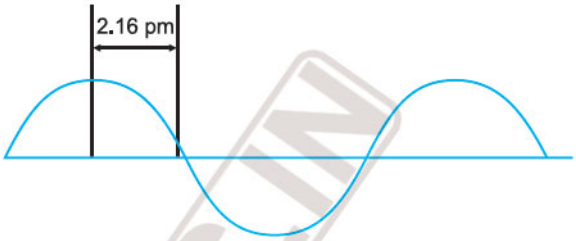

Fig. 1

Ans. Wave length is the distance between the successive crests.

$\therefore$ Wavelength, $\lambda = 4 \times 2.16 = 8.64$ pm

Q.16. Chlorophyll present in green leaves of plants absorbs light at 4.620×10^{14} Hz. Calculate the wavelength of radiation in nanometer. Which part of the electromagnetic spectrum does it belong to ?

Ans. $\lambda = \frac{c}{\nu}$

$$\therefore \quad \lambda = \frac{3.0 \times 10^8}{4.620 \times 10^{14}} = 0.6494 \times 10^{-6}$$

$$= 649.4 \times 10^{-9}\ m = \mathbf{649.4\ nm}$$

It belongs to visible light.

Q.17. What is the difference between the terms 'orbit and orbital' ?

Ans. *Refer Text (Page 45).*

Q.18. Table-tennis ball has a mass 10 g and a speed of 90 m/s. If speed can be measured within an accuracy of 4% what will be the uncertainty in speed and position ?

Ans. Uncertainty in speed of ball $= \frac{90 \times 4}{100} = 3.6\ ms^{-1}$

Uncertainty in position, $\Delta x = \frac{h}{4\pi m \Delta v}$

$$= \frac{6.626 \times 10^{-34} Js}{4 \times 3.14 \times 10 \times 10^{-3} kg \times 3.6\ ms^{-1}}$$

$$= \mathbf{1.46 \times 10^{-33}\ m}$$

Q.19. The effect of uncertainty principle is significant only for motion of microscopic particles and is negligible for the macroscopic particles. Justify the statement with the help of a suitable example.

Ans. *Refer Text*, significance of uncertainty principle *(Page 41)*.

Q.20. Hydrogen atom has only one electron, so mutual repulsion between electrons is absent. However,

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in multielectron atoms, mutual repulsion between the electrons is significant. How does this affect the energy of an electron in the orbitals of the same principal quantum number in multielectron atoms ?

Ans. In case of H-atom, the energies of electron in different orbitals depend only on the value of n. Hence, different orbitals of same shell have same energy. However, in case of multielectron atoms, the energies of the orbitals depend upon $n + l$ values. Hence, for the same value of n but different values of l *i.e.*, different subshells belonging to the same main shell have different energies.

Long Answer Questions *Carrying 5 marks*

Q.21. What is photoelectric effect? State the result of photoelectric effect experiment that could not be explained on the basis of laws of classical physics. Explain this effect on the basis of quantum theory of electromagnetic radiations.

Ans. *Refer Text (Page 14–16).*

Q.22. Threshold frequency, ν_0 is the minimum frequency which a photon must possess to eject an electron from a metal. It is different for different metals. When a photon of frequency 1.0×10^{15} s^{-1} was allowed to hit a metal surface, an electron having 1.988×10^{-19} J of kinetic energy was emitted. Calculate the threshold frequency of this metal. Show that an electron will not be emitted if a photon with a wavelength equal to 600 nm hits the metal surface.

Ans. $h\nu = h\nu_0 + \frac{1}{2}mu^2$

or $h\nu_0 = h\nu - \frac{1}{2}mu^2$

$= 6.63 \times 10^{-34} \times 1.0 \times 10^{15} - 1.988 \times 10^{-19}$

$= 6.63 \times 10^{-19} - 1.988 \times 10^{-19}$

$= 4.642 \times 10^{-19}$ J

$\therefore \quad \nu_0 = \frac{4.642 \times 10^{-19}\ \text{J}}{6.63 \times 10^{-34}\ \text{Js}} = 6.988 \times 10^{14}\ \text{s}^{-1}$

Now frequency of photon of wavelength 600 nm = 600×10^{-9} m

$\nu = \frac{3.0 \times 10^{8}\ \text{ms}^{-1}}{600 \times 10^{-9}\ \text{m}} = 5.0 \times 10^{14}\ \text{s}^{-1}$

Since frequency of photon is less than υ_0, electron will not be emitted.

Q.23. When an electric discharge is passed through hydrogen gas, the hydrogen molecules dissociate to produce excited hydrogen atoms. These excited atoms emit electromagnetic radiation of discrete frequencies which can be given by the general formula.

$$\bar{\nu} = 109677\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

What points of Bohr's model of an atom can be used to arrive at this formula? Based on these points derive the above formula giving description of each step and each term.

Ans. The following two points of Bohr's model can be used to derive the given formula :

(*i*) Electrons revolve around the nucleus in definite energy levels called orbits.

(*ii*) Energy is emitted or absorbed only when electron jumps from one orbit to another.

Derivation

(*i*) According to Bohr, energy of an electron in the n^{th} level is given as

$$E_n = -\frac{2\pi^2 me^4}{n^2h^2}$$

where m = mass of electron, e = charge of electron, h = Planck's constant.

(*ii*) When electron jumps from outer orbit (n_2) to inner orbit (n_1), then difference in energy (ΔE) is emitted as :

$$\Delta E = E_2 - E_1$$

$$= -\frac{2\pi^2 me^4}{n_2^2h^2} - \left(-\frac{2\pi^2 me^4}{n_1^2h^2}\right)$$

$$= \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Now, $\Delta E = h\nu = h\frac{c}{\lambda} = hc\bar{\nu}$

or $\bar{\nu} = \frac{\Delta E}{hc} = \frac{2\pi^2 me^4}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

Substituting the values of c, h, π, m, e in CGS units, we get

$$\bar{\nu} = 109677\ \text{cm}^{-1}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Q.24. Calculate the energy and frequency of the radiation emitted when an electron jumps from $n = 3$ to $n = 2$ in a hydrogen atom.

Ans. $\bar{\nu} = 109677\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\text{cm}^{-1}$

For $n_1 = 2, \quad n_2 = 3$

$\bar{\nu} = 109677\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$

$= 109677 \times \frac{5}{36} = 15232.9\ \text{cm}^{-1}$

$\Delta E = h\nu$

$= \frac{hc}{\lambda} = hc\bar{\nu}$

$= (6.626 \times 10^{-34}\ \text{Js})\,(3.0 \times 10^{10}\ \text{cm s}^{-1}) \times (15232.9\ \text{cm}^{-1})$

$= \mathbf{3.028 \times 10^{-19}\ J}$

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$$\nu = \bar{c}\bar{\nu}$$
$$= (3.0 \times 10^{10}\ \text{cm s}^{-1}) \times 15239.9\ \text{cm}^{-1}$$
$$= 4.57 \times 10^{14}\text{s}^{-1}$$

Q.25. Why was a change in the Bohr model of atom required? Due to which important develop-ment (s), concept of movement of an electron in an orbit was replaced by the concept of probability of finding electron in an orbital ? What is the name given to the changed model of atom ?

Ans. According to Bohr's model, electrons move along fixed circular paths called orbits. Therefore, position and velocity of electron can be well defined. This was contradicted by de Broglie concept of dual nature of electron and Heisenberg's uncertainty principle. Therefore, to incorporate the two principles, the well defined orbits were replaced by regions of maximum probability called orbitals. The changed concept formed the basis of wave mechanical model of atom.

QUICK MEMORY TEST

A. Say True or False

1. 2*s* orbital has one node.
2. Phosphorus (Z = 15) has three unpaired electrons.
2. Fe^{3+} ion has four unpaired electrons.
4. Number of radial nodes in 5*f* orbital is four.
5. It takes less energy to ionize (or remove) an electron from first excited state than the ground state of H-atom.
6. Paschen, Brackett and Pfund series fall in infra red region.
7. The splitting of spectral lines in electrical field is called Zeeman effect.
8. Electronic energy is negative because electron has negative charge.
9. ψ^2 represents probability density.
10. Heisenberg principle is applicable to microscopic objects.
11. 3*s* and 4*p* orbitals have same number of radial nodes.
12. Angular momentum for 2*p* and 3*p* orbital is same.
13. Copper (I) is diamagnetic.
14. Spin quantum number is not originated from Schrodinger wave equation.
15. The de-Broglie wavelength associated with hydrogen atom is larger than that of deuterium atom if both are travelling at the same speed.

B. Complete the missing links

1. Out of 5*d*, 2*f*, 3*d*, 5*s*, the subshell which does not make sense is .....
2. For $n = 3$, the total number of orbitals is .....
3. There are ..... orbitals corresponding to $l = 2$.
4. Dual character of electrons was verified by ..... and ..... .
5. The series in hydrogen spectrum falling in visible region is ..... series.
6. The number of unpaired electrons in Fe^{2+} is ..... .
7. The limiting line of any spectral series in the hydrogen spectrum is the line when n_2 in the Rydberg's formula is .....
8. Lyman series of hydrogen spectrum lies in ..... region.
9. The quantum number which tells about the orientation of different orbitals of an atom is called ..... .
10. The quantum number which describes the subshells present in any main shell is called ..... .

C. Choose the correct alternative

1. The subshell having $n = 5$ and $l = 3$ is *5f/5d*.
2. Total number of electrons in a *d* subshell having $s = +\frac{1}{2}$ is *5/10*.
3. Among 4*d*, 4*f*, 5*s*, and 5*p*, the subshell having largest energy in a multielectron atom is *5s/4f*.
4. The lowest value of *n* that allows '*g*' orbitals to exist is *5/4*.
5. For 2*p* orbitals, the angular quantum number is *1/2*.
6. The number of electrons in a given principal energy level is $2n^2/n^2$.
7. The number of unpaired electrons in chromium atom (Z = 24) is 4/6.
8. For 4*d* subshell, the value of *l* is 2/3.
9. Number of electrons having $n = 4$ and $m_s = +\frac{1}{2}$ are *10/16*.
10. ψ^2 represents *probability/probability density*.
11. Number of radial nodes in 4*f* orbital is *0 / 1*.
12. Copper (II) ion is *paramagnetic / diamagnetic*.
13. An orbital has *l/n – l* angular nodes.
14. The wavelength associated with a proton is *less/more* than that of electron.
15. 5*s* orbital has *5/4* radial nodes.
16. The angular momentum for 3*s* orbital is *0/3*.

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Answers QUICK MEMORY TEST

A. Say True or False

1. True
2. True
3. **False.** Fe^{3+} ion has five unpaired electrons.
4. **False.** $(n - l - 1)$ i.e. $(5 - 3 - 1) = 1$ node.
5. True
6. True
7. **False.** Zeeman effect is the splitting of the spectral lines in magnetic field.
8. False
9. True
10. **False.** Heisenberg principle is applicable to all objects but has significance only for microscopic bodies.
11. **True.** Both have 2 radial nodes.
12. **True.** Because angular momentum depends only upon the value of l as $\sqrt{l(l+1)}\,\frac{h}{2\pi}$.
13. True
14. True
15. True.

B. Complete the missing links

1. $2f$
2. Nine
3. Five
4. Davisson and Germer, Thomson
5. Balmer
6. 4
7. 6
8. uv
9. magnetic quantum number
10. azimuthal quantum number.

C. Choose the correct alternative

1. $5f$
2. 5
3. $5s$
4. 5
5. 1
6. $2n^2$
7. 6
8. 2
9. 16
10. probability density
11. 0
12. paramagnetic
13. l
14. less
15. 4
16. 0

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. How did wave mechanical model of an atom overruled the circular orbits proposed by Bohr ?

Ans. The wave mechanical model of an atom was proposed by Schrodinger in terms of mathematical equation known as Schrodinger wave equation. The solution of this equation gives wave function ψ and the square of the wave function, *i.e.*, ψ^2 measures the probability density of finding the electron. So, according to this model, it is possible to locate the regions around the nucleus where the probability of finding the electron is maximum. These regions where the probability of finding the electron is maximum are called **orbitals**. Thus, wave mechanical model leads to the concept of orbital.

This concept overruled the idea of circular orbits proposed by Bohr. According to Bohr's model of an atom, the electrons revolve around the nucleus in certain well defined circular paths called orbits. This means that electron remains only in the circular orbits at a definite distance from the nucleus. However, according to wave mechanical model, there are regions where the probability of finding the electrons is maximum. The electron may be even outside this regions.

Q.2. Which of the following sets of orbitals are degenerate and why ?

(*i*) 1*s*, 2*s*, and 3*s* in Mg atom
(*ii*) $2p_x$, $2p_y$ and $2p_z$ in C atom
(*iii*) 3*s*, $3p_x$ and 3*d* orbitals in H atom .

Ans. (*i*) 1*s*, 2*s* and 3*s* orbitals in Mg atom are not degenerate because these have different values of n.

(*ii*) $2p_x$, $2p_y$ and $2p_z$ orbitals in C atom are degenerate because these belong to same subshell.

(*iii*) 3*s*, $3p_x$ and 3*d* orbitals in H atom are degenerate because for H atom, the subshells having same value of n have same energies.

Q.3. An electron in a hydrogen atom is excited from the ground state to the $n = 4$ state. Predict which of the following statements are true or false:

(*i*) $n = 4$ is the first excited state.

(ii) It takes more energy to ionize (remove) the electron from $n = 4$ than in the ground state.

(iii) The wavelength of light emitted when the electron drops from $n = 4$ to $n = 2$ is longer than that from $n = 4$ to $n = 1$.

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(*iv*) The wavelength which the atom absorbs in going from $n = 1$ to $n = 4$ is the same as emitted when it goes from $n = 4$ to $n = 1$.

(*v*) The electron is farther from the nucleus (on average) in $n = 4$ than in the ground state.

Ans. (*i*) False (*ii*) False (*iii*) True (*iv*) True (*v*) True.

Q.4. If uncertainty in position of a moving electron is equal to its de-Broglie wavelength, show that its velocity is completely uncertain.

Ans. By de-Broglie equation :

$$\lambda = \frac{h}{p}$$

But, $\lambda = \Delta x$ (given)

$$\therefore \quad \Delta x = \frac{h}{p}$$

According to Heisenberg uncertainty principle,

$$\Delta x \,.\, \Delta p \geq \frac{h}{4\pi}$$

$$\frac{h}{p}.\Delta p \geq \frac{h}{4\pi}$$

or $$\frac{h}{mv}.m\Delta v \geq \frac{h}{4\pi}$$

or $$\frac{\Delta v}{v} \geq \frac{1}{4\pi}$$

or $$\Delta v \geq \frac{v}{4\pi}$$

Thus, uncertainty in velocity is so large that its velocity is uncertain.

Q.5. Show that ground state energy of an electron in H-atom is equal to the first excited state energy of electron in He^+ ion (assuming their Rydberg's constants to be equal).

Ans. Energy of electron in nth shell is

$$E_n = -R_H\frac{Z^2}{n^2}$$

$$= -13.60\frac{Z^2}{n^2}\text{ eV}$$

For H-atom in the ground state, $n = 1$ and $Z = 1$

$$\therefore \quad E_1 = -13.60 \text{ eV}$$

For He^+ ion in the first excited state, $Z = 2$, $n = 2$

$$\therefore \quad E_2 = -13.60 \times \frac{2^2}{2^2} = -13.60\ eV$$

Q.6. What is the difference in the orbital angular momentum of 2*p* and 3*p* electron ? Explain.

Ans. Orbital angular momentum is given as :

Orbital angular momentum

$$= \frac{h}{2\pi}\sqrt{l(l+1)}$$

Since it is independent of the principal quantum number '*n*' and depends only on the azimuthal quantum number '*l*', it will be same for 2*p* and 3*p* electron. Hence, there will be no difference.

Q.7. Predict the number of nodes and nodal planes in (*i*) $3p_x$ (*ii*) 4*s* and (*iii*) $3d_{x^2-y^2}$ orbital.

Ans.

No. of radial nodes $= n - l - 1$ and

No. of nodal planes $= l$

$\therefore$	Nodes	Nodal planes
(*i*) $3p_x$	1	1
(*ii*) 4*s*	3	0
(*iii*) $3d_{x^2-y^2}$	0	2

Q.8. What will become to the wavelength associated with a moving particle if its velocity is doubled ?

Ans. Wavelength becomes half of the original value $\left(\lambda = \frac{h}{mv}\right)$.

Q.9. Cu^{2+} is more stable than Cu^+ in aqueous solution. Explain.

Ans. Cu^+ has outermost electronic configuration as $3d^{10}$ and therefore, should be most common and most stable state because of extra stability associated with completely filled *d*-subshell (d^{10}). However, this is not true and Cu^{2+} with outer electronic configuration $3d^9$ is more stable than Cu^+. This is due to **high hydration energy in aqueous solution and high lattice energy in solid state of Cu^{2+} as compared to Cu^+.** The equilibrium :

$$2\,Cu^+ \rightleftharpoons Cu^{2+} + Cu$$

$$K = \frac{\left[Cu^{2+}\right]}{\left[Cu^+\right]^2} = 1.6\times10^6$$

The constant for disproportionation of Cu^+ in aqueous solution shows that Cu^{2+} is very stable in aqueous solution as compared to Cu^+.

Q.10. How do $d_{x^2-y^2}$ and d_{xy} orbitals differ in their orientation in space ?

Ans. The four lobes of $d_{x^2-y^2}$ lie on the X and Y axis while the lobes of d_{xy} lie in between X and Y axis (*i.e.* at an angle of 45°). So, $d_{x^2-y^2}$ orbital is exactly like d_{xy} except that it is rotated through 45° around Z–axis.

Q.11. For H atom the Bohr radius for first orbit is 0.529Å and the radius of maximum probability for H-atom according to wave mechanical model is also 0.529Å. How do the two approaches differ ?

Ans. Bohr predicted that the electron will always be found moving around the nucleus in a circular path of radius 0.529 Å. According to his model, electron cannot be found at distance less than or more than 0.529 Å. However according to wave mechanical model, electron is most likely to be found at this distance but there is definite probability of finding the electron at distances both shorter and larger than 0.529 Å. In other words, according to wave mechanical model, the electron keeps on moving towards or away from the nucleus and the maximum probability of locating it is at a radius of 0.529 Å from the nucleus. Fig. (*a*) shows the electron cloud picture of

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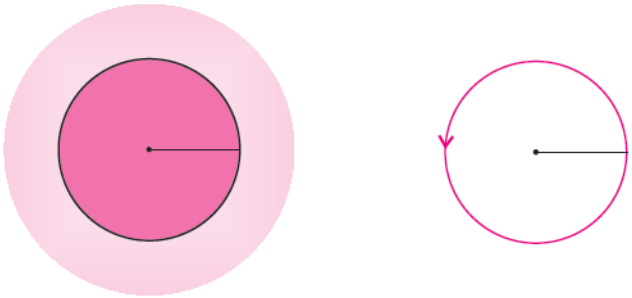
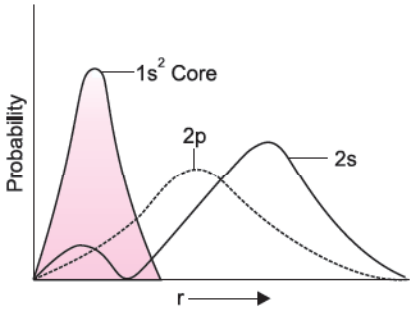
1*s*-orbital having radius of maximum probability and Fig. (*b*) gives the Bohr picture of orbit in which electron is found only at this distance.



(a) Radius of maximum probability (0.529 Å) (b) Bohr radius (0.529 Å)

Q.12. For a multielectron atom, the maximum of 2*p*-orbital in radial probability distribution graph is nearer the nucleus than that of 2*s*-orbital. Therefore, 2*p*-orbital should be closer to the nucleus and lower in energy than 2*s*-orbital. But 2*s*-orbital has lower energy than 2*p*-orbital. Explain.

Ans. The radial probability distribution graphs for 2*s*- and 2*p*- orbitals are shown below :



It is clear from the figure that in case of 2*s*-orbital, there is a small additional peak or hump. This indicates that a 2*s*-electron spends some of its time near the nucleus. In other words, 2*s*-electron penetrates the 1*s*^{2}-core (or K shell, shown shaded in the figure). Due to penetration, a 2*s*-electron gets less shielding from other electrons and therefore, feels more nuclear charge. As a result, a 2*s*-electron is attracted more strongly by the nucleus than a 2*p*-electron. Thus, 2*s* has lower energy than a 2*p*-electron.

13. For which hydrogen like ion the wavelength difference between the first lines of the Lyman and Balmer series is equal to 59.3 nm ?

Ans. For a spectral line,

$$\frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

For Lyman line,

$$\frac{1}{\lambda_{Lyman}} = RZ^2\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{3RZ^2}{4}$$

$$\text{or} \quad \lambda_{Lyman} = \frac{4}{3\,RZ^2}$$

For Balmer line

$$\frac{1}{\lambda_{Balmer}} = RZ^2\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{5RZ^2}{36}$$

$$\text{or} \quad \lambda_{Balmer} = \frac{36}{5\,RZ^2}$$

$$\lambda_{Balmer} - \lambda_{Lyman} = \frac{36}{5\,RZ^2} - \frac{4}{3\,RZ^2}$$

$$\Rightarrow 59.3 \times 10^{-7}\text{ cm} = \frac{1}{RZ^2}\left[\frac{36}{5} - \frac{4}{3}\right]$$

$$\Rightarrow 59.3 \times 10^{-7} = \frac{1}{109677.8\,Z^2}\left[\frac{108-20}{15}\right]$$

$$= 59.3 \times 10^{-7}$$

$$\text{or} \quad Z^2 = \frac{1}{109677.8} \times \frac{88}{15 \times 59.3 \times 10^{-7}} = 9$$

or $Z = 3$. This corresponds to Li^{2+} ion.

Q. 14. Calculate the wavelength of radiation emitted producing a line in Lyman series when an electron falls from fourth energy level in hydrogen atom. ($R_H = 1.1 \times 10^7\ m^{-1}$)

Ans. According to Rydberg equation,

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For Lyman series, $n_1 = 1$ and $n_2 = 4$

$$\therefore \quad \frac{1}{\lambda} = 1.1 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{4^2}\right) m^{-1}$$

$$\frac{1}{\lambda} = 1.1 \times 10^7 \times \frac{15}{16}$$

$$\text{or} \quad \lambda = \frac{1 \times 16}{1.1 \times 10^7 \times 15} = 9.70 \times 10^{-8}\text{ m}$$

or λ = **97.0 nm.**

Q.15. Calculate the velocity (cm s^{-1}) of an electron placed in third orbit of the hydrogen atom. Also calculate the number of revolutions per second that this electron makes around the nucleus.

Ans. Velocity of electron is given as :

$$v = \frac{2\pi e^2}{nh}$$

Now, $e = 4.8 \times 10^{-10}$ e.s.u., $n = 3$, $h = 6.63 \times 10^{-27}$ erg sec

$$\therefore \quad v = \frac{2 \times 22 \times (4.8 \times 10^{-10})^2}{7 \times 3 \times 6.63 \times 10^{-27}}$$

$$= 7.27 \times 10^7\text{ cm s}^{-1}$$

$$\text{No. of revolutions per second} = \frac{\text{Velocity}}{\text{Circumference}}$$

$$= \frac{v}{2\pi r}$$

$$\text{but} \quad r = \frac{4\pi^2 me^2}{n^2h^2}$$

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$$\therefore \text{ No. of revolutions } = \frac{2\pi e^2}{nh} \times \frac{4\pi^2 me^2}{2\pi n^2 h^2}$$

$$= \frac{4\pi^2 me^4}{n^3 h^3}$$

$$= \frac{4 \times \left(\frac{22}{7}\right)^2 \times \left(9.1 \times 10^{-28}\right) \times \left(4.8 \times 10^{-10}\right)^4}{3^3 \times (6.626 \times 10^{-24})^3}$$

$$= \mathbf{2.42 \times 10^{14}}.$$

16. Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral line of largest energy in the visible region of its atomic spectrum. ($R_H = 1.1 \times 10^7\ m^{-1}$, $c = 3 \times 10^8\ m\ s^{-1}$, $h = 6.62 \times 10^{-34}\ J\ s$)

Ans. The spectral line in visible region corresponds to Balmer series *i.e.* $n_1 = 2$ and $n_2 = 3$ for lowest energy.

$$\text{Now, } \bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= 1.1 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{3^2}\right) m^{-1}$$

$$= 1.1 \times 10^7 \left(\frac{1}{4} - \frac{1}{9}\right)$$

$$= 1.1 \times 10^7 \times \frac{5}{36}$$

$$\therefore \lambda = \frac{36}{1.1 \times 10^7 \times 5}$$

$$= 6.55 \times 10^{-7}\ m$$

$$\text{Now, } E = h\nu = \frac{hc}{\lambda}$$

$$= \frac{6.62 \times 10^{-34} \times 3.0 \times 10^8}{6.55 \times 10^{-7}}$$

$$= 3.03 \times 10^{-19}\ J$$

1 gm atom of hydrogen = 6.02×10^{23} atoms

$\therefore$ Energy corresponding to 1 gram atom of H = $3.03 \times 10^{-19} \times 6.02 \times 10^{23}$

$$= 18.25 \times 10^4\ J$$

$$= \mathbf{182.5\ kJ}$$

Q.17. What is the distance of separation between second and third orbits of H-atom ?

Ans. Radius of nth orbit of H-atom is given as :

$$r_n = 0.529 \times n^2\ \text{Å}$$

$$r_3 = 0.529 \times 3^2 = 0.529 \times 9$$

$$r_2 = 0.529 \times 2^2 = 0.529 \times 4$$

$$\therefore r_3 - r_2 = 0.529\ (9 - 4)\text{Å} = 2.645\ \text{Å}$$

Q.18. Calculate the product of uncertainties in displacement and velocity for an electron of mass 9.1×10^{-31} kg according to Heisenberg's uncertainty principle. ($h = 6.6 \times 10^{-34}\ kg\ m^2\ s^{-1}$).

Ans. According to Heisenberg's uncertainty principle,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

$$\text{or } \Delta x \times m\,\Delta v \geq \frac{h}{4\pi} \quad (\because m \text{ is constant})$$

$$\text{or } \Delta x \times \Delta v \geq \frac{h}{4m\pi}$$

$$m = 9.1 \times 10^{-31}\text{kg}, h = 6.6 \times 10^{-34}\text{kg m}^2\ \text{s}^{-1},$$

$$\pi = 3.14$$

$$\therefore \Delta x \times \Delta v \geq \frac{6.6 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{4 \times \left(9.1 \times 10^{-31}\text{kg}\right) \times 3.14}$$

$$\text{or } \Delta x \times \Delta v \geq \frac{6.6}{4 \times 9.1 \times 3.14} \times 10^{-3}\ \text{m}^2\text{s}^{-1}$$

$$\text{or } \Delta x \times \Delta v \geq 5.77 \times 10^{-5}\ \text{m}^2\ \text{s}^{-1}$$

Thus, product of uncertainties in position and velocity of an electron is equal to or greater than $\mathbf{5.77 \times 10^{-5}\ m^2\ s^{-1}}$.

Q.19. Which state of the triple ionized beryllium (Be^{3+}) has the same orbit radius as that of the ground state of hydrogen atom ?

Ans. For H-atom, radius of ground state is

$$r_1 = \frac{h^2}{4\pi^2 me^2} \quad \ldots(i)$$

For hydrogen like atom,

$$r'_n = \frac{n^2 h^2}{4\pi^2 mZe^2} \quad \ldots(ii)$$

Dividing Eq. (*ii*) by Eq. (*i*)

$$\frac{r'_n}{r_1} = \frac{n^2}{Z}$$

For Be^{3+} ion, Z = 4

$$\therefore \frac{r'_n}{r_1} = \frac{n^2}{4}$$

Now, $r'_n = r_i$

$\therefore$ $n^2 = 4$ or $n = 2$

Thus, the second orbit of Be^{3+} has the same radius as the Bohr's radius of hydrogen atom.

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Q.20. The threshold wavelength for emitting photons from a metal is 6.0×10^3 Å. What would be the wavelength of radiation to produce photoelectrons having twice the kinetic energy of those produced by radiation of wavelength 3×10^3 Å ?

Ans. K.E. of photoelectrons emission is :

$$\text{K.E.} = h\nu - h\nu_0 = \frac{hc}{\lambda} - \frac{hc}{\lambda_0}$$

or $$\text{K.E.} = hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$$

K.E. of electrons emitted by using $\lambda = 3 \times 10^3$ Å or 3000Å

$$\text{K.E.} = hc\left(\frac{1}{3000} - \frac{1}{6000}\right) \quad (\because \lambda_0 = 6000 \text{ Å})$$

K.E. of electrons by using wavelength λ (to be calculated)

$$(\text{K.E.})_2 = hc\left(\frac{1}{\lambda} - \frac{1}{6000}\right)$$

Now, $$(\text{K.E.})_2 = 2(\text{K.E.})_1$$

$$hc\left(\frac{1}{\lambda} - \frac{1}{6000}\right) = 2hc\left(\frac{1}{3000} - \frac{1}{6000}\right)$$

or $$\frac{1}{\lambda} = \frac{2}{3000} - \frac{1}{3000} + \frac{1}{6000} = \frac{1}{2000}$$

$\therefore$ $$\boldsymbol{\lambda = 2000 Å}$$

Q.21. The angular momentum of an electron in Bohr's orbit of H-atom is 3.02×10^{-34} kg m^2 s^{-1}. Calculate the wavelength of the spectral line emitted when the electron jumps from this level to the next lower level.

Ans. Angular momentum (mvr)

$$= n\frac{h}{2\pi} = 3.02 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$$

$$n = 3.02 \times 10^{-34} \times \frac{2\pi}{h}$$

$$= \frac{3.02 \times 10^{-34} \times 2 \times 3.14}{6.3 \times 10^{-34}} = 3$$

When the electron jumps from $n = 3$ to $n = 2$, the wavelength of spectral line,

$$\frac{1}{\lambda} = 109677\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$$= 109677\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$\frac{1}{\lambda} = 109677 \times \frac{5}{36}$$

or $$\lambda = \frac{36}{5 \times 109677}$$

$$= \mathbf{6.56 \times 10^{-5} \text{ cm} \quad \text{or} \quad 656 \text{ nm}.}$$

Q.22. An electron in certain Bohr orbit has velocity 1/275 of the velocity of light. Calculate the orbit in which the electron is revolving.

Ans. Velocity of electron

$$= \frac{1}{275} \times 3.0 \times 10^{10} \text{ cm s}^{-1}$$

$$= 1.09 \times 10^8 \text{ cm s}^{-1}$$

Velocity of electron in nth orbit,

$$v_n = \frac{2\pi Ze^2}{nh}$$

$Z = 1$, $e = 4.80 \times 10^{-10}$ esu, $h = 6.63 \times 10^{-27}$ erg sec

$$v_n = \frac{2 \times 3.14 \times 1 \times \left(4.80 \times 10^{-10}\right)^2}{n \times \left(6.3 \times 10^{-27}\right)}$$

$$= \frac{2.30 \times 10^8}{n}$$

$\therefore$ $$\frac{2.30 \times 10^8}{n} = 1.09 \times 10^8 \text{ cm s}^{-1}$$

$\therefore$ $$n = \frac{2.30 \times 10^8}{1.09 \times 10^8} = 2$$

$\therefore$ $$n = 2$$

Revision Exercises

Very Short Answer Questions *Carrying 1 marks*

1. What is the difference between a quantum and a photon?
2. Can an electron have the quantum number values as $n = 2$, $l = 2$ and $m = +2$?
3. How many sub-levels are there in M shell ? What are their designations ?
4. What quantum numbers n and l are assigned to a $3p$-orbital ?
5. Write the electronic configuration of chromium ($Z = 24$).
6. An atom of an element has 19 electrons. What is the total number of p-electrons ?

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7. What is the sequence of energies of 3*s*, 3*p* and 3*d*-orbitals in
   (i) a hydrogen atom, and
   (ii) a multielectron atom ?
8. According to which principle an atom cannot have more than two electrons ?
9. What designations are given to the following subshells having:
   (i) $n = 4, l = 3$
   (ii) $n = 3, l = 2$
10. If $n = 3$, what are values of quantum number l?
11. What is the relation between the shapes of $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals?
12. How many electrons are present in 3*d* orbitals in chromium ($Z = 24$)?
13. If the quantum number '*l*' has a value of 2, what are the permitted values of quantum number *m* ?
14. How many electrons *s* and *p*-subshell can accommodate ?
15. Which energy levels do not have *p*-orbital ?
16. What do you mean by saying that energy of electron is quantized ?
17. Out of electron and proton which one will have, a higher velocity to produce matter waves of the same wavelength ? Explain it.
18. What is the total number of orbitals associated with principal quantum number, $n = 3$?
19. Arrange 3*s*, 3*p* and 3*d* orbitals in the increasing order of energy for hydrogen atom.
20. The atomic number of an element is 20. How many electrons have $l = 0$ in this ?
21. Define Hund's rule of maximum multiplicity.
22. Define Pauli exclusion principle.

Short Answer Questions *Carrying 2 or 3 marks*

1. List some important postulates of Bohr's model of an atom.
2. How does the existence of line spectra support for the Bohr model of the atom ?
3. Why was Bohr model abandoned ?
4. In terms of Bohr theory of the structure of the atom, why is it that electrons do not spiral into the nucleus ?
5. Name the three quantum numbers which are necessary to describe an orbital. What are the permitted values for these ?
6. What is the maximum number of electrons in :
   (i) a principal quantum number
   (ii) an orbital
   (iii) *p*-subshell
   (iv) *s*, *p* and *d*-subshells in an atom ?
7. Give the number of orbitals in :
   (i) a *p*-subshell
   (ii) a *d*-subshell
   (iii) second shell.
8. Describe the orbital with the following quantum numbers :
   (i) $n = 1, l = 0$ *(ii)* $n = 2, l = 1, m = 0$
   (iii) $n = 3, l = 2$ *(iv)* $n = 4, l = 1$
   (v) $n = 3, l = 0, m = 0$ *(vi)* $n = 3, l = 1$
9. Give the electronic configurations of :
   (i) Scandium (Z = 21)
   (ii) Chromium (Z = 24).
10. How many orbitals and how many electrons are there in each of the first two principal quantum numbers ?
11. Give the electronic configurations of the following ions :
    (i) H^- *(ii)* Na^+
    (iii) F^- *(iv)* Mg^{2+}.
12. Fill in the blanks :
    (i) The size of an orbital is dependent on the value of .....
    (ii) The orbitals having the same energies are called .....
    (iii) The number of unpaired electrons in carbon is ..... and in nitrogen is .....
    (iv) The shape of 1*s*-orbital is ..... .
    (v) ..... filled orbitals have extra stability.
13. Define Aufbau principle. Which of the following orbitals are possible ?
    1*p*, 2*s*, 2*p* and 3*f*
14. With the help of Pauli's exclusion principle and the concept of atomic numbers for orbitals, show that an M shell cannot accommodate more than 18 electrons.
15. What is an orbital ? How will you differentiate between an orbit and an orbital ?
16. Compare the shapes of 1*s*- and 2*s*-orbitals.
17. What is the difference between the symbols *l* and L ?
18. How many electrons are there in the valence quantum level of copper (atomic number = 29) atom ? Give reasons.
19. Write the electronic configurations of the following elements :
    Carbon (Z = 6), neon (Z = 10), magnesium (Z = 12), chlorine (Z = 17), calcium (Z = 20), chromium (Z = 24), iron (Z = 26) and rubidium (Z = 37).
20. Identify the atoms that have the following ground state electronic configurations :
    (i) $1s^2\ 2s^2\ 2p^6\ 3s^2$
    (ii) $1s^2\ 2s^2\ 2p^5$
    (iii) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$.

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21. In building up of the atoms, the filling of 4*s*-orbital takes place before the 3*d*-orbital. Explain.

22. The expected electronic configuration of copper is [Ar] $3d^9\ 4s^2$ though actually it is [Ar] $3d^{10}\ 4s^1$. Give reasons.

23. An atom of an element has 19 electrons. Find out :

(*a*) its atomic number

(*b*) total number of *s*-electrons

(*c*) total number of *p*-electrons.

24. Give the shapes of *s* and *p*-orbitals.

25. What is Hund's rule of maximum multiplicity ? Illustrate this by taking the example of carbon.

26. Explain why half-filled and completely-filled orbitals have extra stability.

27. What is Aufbau principle ? Write the electronic configurations of the elements of atomic numbers 16, 20, 24 and 35.

28. Draw the shape of an orbital which has $l = 0$.

29. State Aufbau principle. Write electronic configurations of the elements with atomic numbers 17 and 24.

30. Why in the building of the atom, the filling of 4*s*-orbital takes place before 3*d*-orbital ?

31. State and explain Pauli's exclusion principle. Write the electronic configuration of the element with atomic number 24.

32. What is Hund's rule of maximum multiplicity ? Explain by taking an example of nitrogen.

33. Discuss the significance of magnetic quantum number.

34. What is the experimental evidence in support of the idea that electronic energies in an atom are quantized ?

35. The effect of uncertainty principle is significant only for motion of microscopic particles and is negligible for the macroscopic particles. Justify the statement with the help of a suitable example.

Long Answer Questions *carrying 5 marks*

1. Give the essential postulates of Bohr's model of an atom. How did it explain

(*i*) the stability of an atom

(*ii*) origin of spectral lines in hydrogen atom ?

2. What are quantum numbers ? What permitted values can these have ? Give the significance of each quantum number.

3. What is photoelectric effect ? State the result of photoelectric effect experiment that could not be explained on the basis of laws of classical physics. Explain this effect on the basis of quantum theory of electromagnetic radiations.

4. Why was a change in the Bohr Model of atom required? Due to which important development (s), concept of movement of an electron in an orbit was replaced by, the concept of probability of finding electron in an orbital ? What is the name given to the changed model of atom?

5. (*a*) What is radial probability distribution curve? Draw radial probability distribution curves for 1*s* and 2*s* orbitals.

(*b*) Discuss the similarities and differences between 1*s* and 2*s* orbitals.

(*c*) How many nodes are present in 1*s* and 2*s* orbitals?

6. (*a*) How many orbitals are possible for a *d*-subshell?

(*b*) Draw the shapes of d_{xy} and $d_{x^2-y^2}$ orbitals? What is common between these and what is difference between these orbitals? What is the angle between the lobes of these orbitals?

(*c*) Name a 3*d* orbital which has electron density along all the three axes.

Numerical Problems *carrying 5 marks*

1. What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from the energy level with $n = 4$ to the energy level with $n = 1$? In which region of the electromagnetic spectrum does this radiation fall ?

2. Calculate the wave number of the radiation emitted when an electron in a hydrogen atom undergoes a transition from 4th energy level to the 2nd energy level.

3. In the Balmer series of atomic spectra of hydrogen atom, a line corresponding to wavelength 656·4 nm was obtained. Calculate the number of higher orbit from which the electron drops to produce this line.

4. Calculate the wavelength (in nanometers) emitted by a photon during a transition from $n = 6$ to $n = 4$ state in the H-atom.

5. Calculate the wavelength associated with a H-atom (mass = 1.676×10^{-27} kg) moving with velocity of 8.0×10^2 cm s^{-1}.

6. Calculate the value of $\Delta x \cdot \Delta v$ for an electron (mass of electron = 9.1×10^{-31} kg).

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Hints & Answers for Revision Exercises

Very Short Answer Questions

1. The smallest packet of energy of any radiation is called a quantum while that of light is called photon.

2. No

3. Three, $3s$, $3p$, $3d$

4. $n = 3, l = 1$

5. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

6. 12

7. (*i*) $3s = 3p = 3d$
(*ii*) $3s < 3p < 3d$

8. Pauli's exclusion principle

9. (*i*) $4f$ (*ii*) $3d$

10. For $n = 3$, $l = 0, 1, 2$

11. Rotation of 45° around X and Y axis of d_{xy} orbital gives $d_{x^2-y^2}$ orbital and vice versa.

12. Cr (Z = 24): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5\ 4s^1$
No. of electrons in $3d$ orbitals = 5.

13. $m = -2, -1, 0, +1, +2$

14. 2, 6

15. First

16. This means that the electrons in an atom have only definite values of energies.

17. Electron ($\lambda = \frac{h}{mv}$ or $v = \frac{h}{m\lambda}$ or $v \propto \frac{1}{m}$ for same λ)

18. Nine

19. $3s = 3p = 3d$

20. Electronic configuration : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
No. of electrons having $l = 0$ (*i.e.* s-orbitals) = 8.

Short Answer Questions

11. Hydrogen, about 1837 times

15. (*i*) $2n^2$ (*ii*) 2 (*iii*) 6 (*iv*) 2, 6, 10

16. (*i*) 3 (*ii*) 5 (*iii*) 4

17. (*i*) $1s$ (*ii*) $2p_z$ (*iii*) $3d$ (*iv*) $4p$ (*v*) $3s$ (*vi*) $3p$

18. (*i*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$
(*ii*) $1s^2\ 2s^2\ 2s^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

20. (*i*) $1s^2$ (*ii*) $1s^2\ 2s^2\ 2p^6$
(*iii*) $1s^2\ 2s^2\ 2p^6$

21. (*i*) principal quantum number
(*ii*) degenerate
(*iii*) two, three
(*iv*) spherical
(*v*) half-filled and completely.

22. $2s$, $2p$

27. [Ar] $3d^{10}\ 4s^1$; one.

28. $1s^2\ 2s^2\ 2p^2$, $1s^2\ 2s^2\ 2p^6$, $1s^2\ 2s^2\ 2p^6\ 3s^2$, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$,
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$,
$1s^2\ 2s^2\ 2p^6\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s^1$.

29. (*i*) Magnesium
(*ii*) fluorine
(*iii*) copper.

32. (*a*) 19 (*b*) 7 (*c*) 12.

36. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$, $1s^2\ 2s^2\ 2p^6\ 4s^1\ 3d^5$, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$.

40. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

41. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$.

Numerical Problems

1. According to Rydberg equation,

$$\frac{1}{\lambda} = 109678 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{cm}^{-1}$$

Here $n_1 = 1$, $n_2 = 4$

$$\therefore \quad \frac{1}{\lambda} = 109678 \left(\frac{1}{1^2} - \frac{1}{4^2}\right) \text{cm}^{-1}$$

$$= 109678 \times \frac{15}{16} \text{cm}^{-1}$$

$$\text{or} \quad \lambda = \frac{16}{109678 \times 15 \text{cm}^{-1}} = 9.72 \times 10^{-6} \text{ cm}$$

$$= 97.2 \times 10^{-9} \text{ m}$$

$$= 97.2 \text{ nm}$$

2. $$\bar{\nu} = \frac{1}{\lambda} = 109678 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{cm}^{-1}$$

Here $n_1 = 2, n_2 = 4$

$$\therefore \quad \bar{\nu} = \frac{1}{\lambda} = 109678 \left(\frac{1}{2^2} - \frac{1}{4^2}\right) \text{cm}^{-1}$$

$$= 109678 \times \frac{12}{16} \text{cm}^{-1} = \mathbf{8.2 \times 10^4\ cm^{-1}}$$

3. $$\frac{1}{\lambda} = 109678 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{cm}^{-1}$$

For Balmer series $n_1 = 2$, $\lambda = 656.4 \times 10^{-9}$ m
$= 656.4 \times 10^{-7}$ cm

$$\frac{1}{656.4 \times 10^{-7} \text{cm}} = 109678 \left[\frac{1}{2^2} - \frac{1}{n_2^2}\right] \text{cm}^{-1}$$

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$$\text{or} \quad \frac{1}{4}-\frac{1}{n_2^2} = \frac{1}{109678\times656.4\times10^{-7}}$$

$$\text{or} \quad \frac{1}{4}-\frac{1}{n_2^2} = \frac{1}{7.20}$$

$$\text{or} \quad -\frac{1}{n_2^2} = \frac{1}{7.20}-\frac{1}{4}$$

$$= \frac{4-7.20}{28.80}=-\frac{3.20}{28.80}$$

$$\text{or} \quad \frac{1}{n_2^2} = \frac{3.20}{28.80} \quad \text{or} \quad n_2^2=\frac{28.80}{3.20}=9$$

$$n_2 = \sqrt{9} = \textbf{3. Third energy level.}$$

4. For transition from $n_i = 6$ to $n_f = 4$,

$$\Delta E = 2.18\times10^{-18}\text{ J}\left(\frac{1}{6^2}-\frac{1}{4^2}\right)$$

$$= 2.18\times10^{-18}\left(\frac{16-36}{16\times36}\right)\text{J}$$

$$= -7.57\times10^{-20}\text{ J}$$

It is emission energy. The frequency of the photon (taking magnitude) of energy,

$$\nu = \frac{\Delta E}{h}=\frac{7.57\times10^{-20}}{6.626\times10^{-34}}=1.142\times10^{14}\text{ s}^{-1}$$

$$\text{or} \quad \lambda = \frac{c}{\nu}=\frac{3.0\times10^{8}\text{ ms}^{-1}}{1.142\times10^{14}}=2.63\times10^{-6}\text{ m}$$

$$\text{or} \quad = \textbf{2.63 × 10}^{\textbf{3}}\textbf{ nm}$$

5. $\lambda = \dfrac{h}{m\nu}$

$$= \frac{6.626\times10^{-34}\text{ Js}}{(1.676\times10^{-27}\text{ kg})\times(8\text{ ms}^{-1})}$$

$$= 4.94\times10^{-8}\text{ m} = \textbf{49.4 nm}$$

6. $\Delta x\cdot\Delta v = \dfrac{h}{4\pi m}=\dfrac{6.626\times10^{-34}}{4\times3.14\times9.1\times10^{-31}}$

$$= 5.797\times10^{-5}\text{ m}^2\text{ s}^{-2}$$

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Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

BOHR MODEL: RADIUS OF ORBIT, ENERGY AND VELOCITY OF AN ELECTRON

According to Bohr model, an electron with charge $-e$ revolves around the nucleus in an orbit of radius r. Let the charge on the nucleus be $+Ze$. For an electron to remain in its orbit, the electrostatic attraction between the electron and the nucleus which tends to pull the electron towards the nucleus must be equal to the centrifugal force which tends to throw the electron out of its orbit.

$$\text{Centrifugal force} = \frac{mv^2}{r}$$

Coulombic force of attraction between nucleus of charge $+Ze$ and electron of charge $-e$ is

$$\text{Coulombic force of attraction} = \frac{Ze\times e}{r^2}=\frac{Ze^2}{r^2}$$

When the two forces balance,

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}$$

$$\text{Hence,} \quad v^2 = \frac{Ze^2}{mr} \qquad ...(i)$$

Radius of Orbit,

According to Bohr's model of an atom, angular momentum is integral multiple of $h/2\pi$,

$$mvr = \frac{nh}{2\pi}$$

$$\text{or} \quad v = \frac{nh}{2\pi mr} \qquad ...(ii)$$

$$\text{or} \quad v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \qquad ...(iii)$$

From eq. (i) and (iii)

$$\frac{Ze^2}{mr} = \frac{n^2h^2}{4\pi^2m^2r^2}$$

$$\text{or} \quad Ze^2 = \frac{n^2h^2}{4\pi^2mr}$$

$$\text{or} \quad r = \frac{n^2h^2}{4\pi^2me^2Z} \qquad ...(iv)$$

Since for hydrogen atom, $Z = 1$, hence the radius of nth orbit of H-atom is

$$r_n = \frac{n^2h^2}{4\pi^2me^2} \qquad ...(v)$$

Energy of Electron

The total energy, E of electron revolving in the nth orbit is equal to the sum of the kinetic

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energy $\left(\frac{1}{2}mv^2\right)$ and the potential energy $\left(\frac{-Ze^2}{r_n}\right)$. Thus,

$$E = \frac{1}{2}mv^2 - \frac{Ze^2}{r_n} \quad ...(vi)$$

From eq. (*i*)

$$mv^2 = \frac{Ze^2}{r_n}$$

Subtracting the value of mv^2 in eq. (*vi*)

$$E = \frac{Ze^2}{2r_n} - \frac{Ze^2}{r_n} = -\frac{Ze^2}{2r_n} \quad ...(vii)$$

Substituting the value of r_n from eq. (*v*) in eq. (*vii*), we get

$$E = -\frac{Ze^2}{2} \times \frac{4\pi^2 Zme^2}{n^2h^2}$$

Thus, the energy of electron in *n*th orbit, E_n may be given as

$$E_n = -\frac{2\pi^2 me^4 Z^2}{n^2h^2} \quad ...(viii)$$

This is the Bohr equation of energy of electron in the *n*th orbit for hydrogen and hydrogen like ions (such as He^+, Li^{2+}, etc.)

Velocity of Electron in an Orbit

Substituting the value of *r* from eq. (*iv*) in eq. (*ii*), we get

$$v = \frac{nh}{2\pi m} \times \frac{4\pi^2 me^2 Z}{n^2h^2}$$

or $$v = \frac{2\pi e^2 Z}{nh} \quad ...(ix)$$

OBJECTIVE TYPE QUESTIONS

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Select the Correct Answers :

Bohr's Model and its Limitations

A1. In the Bohr's orbit, the ratio of total kinetic energy and the total energy of the electron is
(*a*) –2 (*b*) –1
(*c*) +2 (*d*) 0

A2. The spectral line in hydrogen spectrum obtained when the electron jumps from $n = 5$ to $n = 2$ energy level belongs to :
(*a*) Lyman series (*b*) Balmer series
(*c*) Paschen series (*d*) Pfund serties.

A3. The energy of the electron in the *n*th orbit of hydrogen atom is given as :

$$E_n = -\frac{1311.8}{n^2} \text{ kJ mol}^{-1}$$

What is the energy emitted per atom when an electron jumps from third energy level to second energy level ?
(*a*) 329·7 kJ (*b*) $3{\cdot}03 \times 10^{-19}$ J
(*c*) 182·2 kJ (*d*) 145·7 kJ.

A4. The transition in He^+ spectrum from $n = 4$ to $n = 2$ corresponds to which transition in the H atom spectrum ?
(*a*) $n = 2$ to $n = 1$ (*b*) $n = 3$ to $n = 1$
(*c*) $n = 3$ to $n = 2$ (*d*) $n = 4$ to $n = 2$.

A5. The ionization energy of H atom is 13.6 eV. The ionization energy of Li^{2+} ion will be :
(*a*) 54.4 eV (*b*) 40.8 eV
(*c*) 27.2 eV (*d*) 122.4 eV.

A6. The radius of first orbit of hydrogen is 0.53 Å. The radius of second orbit would be :
(*a*) 1.06 Å (*b*) 0.26 Å
(*c*) 0.53 Å (*d*) 2.12 Å.

A7. How many spectral lines are produced in the spectrum of hydrogen atom from 5th energy level ?
(*a*) 5 (*b*) 10
(*c*) 15 (*d*) 4

A8. In Bohr's theory, the radius *r* of orbit is proportional
(*a*) *n* (*b*) n^2
(*c*) n^{-1} (*d*) n^{-2}

A9. What transition in He^+ ion shall have the same wave number as the first line in Balmar series of H atom ?
(*a*) $7 \longrightarrow 5$ (*b*) $5 \longrightarrow 3$
(*c*) $6 \longrightarrow 4$ (*d*) $4 \longrightarrow 2$

A10. The ratio of the difference in energy between the first and the second Bohr orbit to that between second and third Bohr orbit is
(*a*) $\frac{1}{2}$ (*b*) $\frac{1}{3}$
(*c*) $\frac{27}{5}$ (*d*) $\frac{4}{9}$

A11. Which of the following transitions will have minimum wavelength ?
(*a*) $n_2 \longrightarrow n_1$ (*b*) $n_3 \longrightarrow n_1$
(*c*) $n_4 \longrightarrow n_2$ (*d*) $n_4 \longrightarrow n_1$

A12. In hydrogen atom, energy of the first excited state is –3.04 eV. Then find out the K.E. of the same orbit of H-atom.
(*a*) + 3.4 eV (*b*) + 6.8 eV
(*c*) – 13.6 eV (*d*) + 13.6 eV

Answers

A1. (*b*) **A2.** (*b*) **A3.** (*b*) **A4.** (*a*) **A5.** (*d*) **A6.** (*d*) **A7.** (*b*) **A8.** (*b*) **A9.** (*c*) **A10.** (*c*) **A11.** (*d*) **A12.** (*a*)

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A13. The ratio of radii of the first three Bohr orbits of H-atom is

(a) 1 : 2 : 3 (b) 1 : 4 : 9

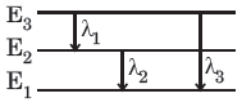
(c) 1 : 3 : 27 (d) $1 : \sqrt{2} : \sqrt{3}$

A14. The ratio of the frequency corresponding to the third line in Lyman series of hydrogen atomic spectrum to that of the first line in Balmer series of Li^{2+} spectrum is

(a) $\frac{4}{5}$ (b) $\frac{5}{4}$

(c) $\frac{4}{3}$ (d) $\frac{3}{4}$

A15. Three energy levels E_1, E_2 and E_3 and the wave lengths produced by transitions are shown below:



Which one of the following relationship is correct?

(a) $\lambda_3 = \lambda_1 + \lambda_2$ (b) $\lambda_1 + \lambda_2 + \lambda_3 = 0$

(c) $\lambda_3 = \frac{\lambda_1\lambda_2}{\lambda_1 + \lambda_2}$ (d) $\lambda_3 = \frac{\lambda_1 + \lambda_2}{\lambda_1\lambda_2}$

Wave Mechanical Model of Atom and Quantum Numbers

A16. The de-Broglie wavelength of an electron is 600 nm. The velocity of the electron is :

($h = 6.6 \times 10^{-34}$ J sec, $m = 9.0 \times 10^{-31}$ kg)

(a) 1.8×10^3 m s^{-1} (b) 1.2×10^5 m s^{-1}

(c) 5.4×10^3 m s^{-1} (d) 1.2×10^3 m s^{-1}

A17. If travelling at same speeds, which of the following matter waves have the shortest wavelength ?

(a) Electron (b) Alpha particle (He^{2+})

(c) Neutron (d) Proton

A18. If uncertainty in the position of an electron is zero, the uncertainty in its momentum would be

(a) zero (b) $\geq \frac{h}{4\pi}$

(c) $< \frac{h}{4\pi}$ (d) infinite

A19. Which of the following orbitals does not make sense ?

(a) 6s (b) 3p

(c) 2d (d) 4f.

A20. Two electrons occupying the same orbital are distinguished by :

(a) spin quantum number

(b) azimuthal quantum number

(c) magnetic quantum number

(d) principal quantum number.

A21. The designation of an orbital with $n = 4$ and $l = 3$ is :

(a) 4s (b) 4p

(c) 4d (d) 4f.

A22. For each value of l, the number of m_s values are :

(a) $2l$ (b) nl

(c) $2l + 1$ (d) $n - l$.

A23. The maximum number of 4d-electrons having spin quantum number $s = +\frac{1}{2}$ are :

(a) 10 (b) 7

(c) 1 (d) 5.

A24. The maximum number of electrons in a subshell is given by the expression :

(a) $4l - 2$ (b) $4l + 2$

(c) $2l + 1$ (d) $2n^2$.

A25. A subshell with $n = 6$, $l = 2$ can accommodate a maximum of :

(a) 10 electrons (b) 12 electrons

(c) 36 electrons (d) 72 electrons.

A26. For which one of the following sets of four quantum numbers an electron will have the highest energy :

	n	l	m	s
(a)	3	2	1	1/2
(b)	4	1	0	−1/2
(c)	4	2	−1	1/2
(d)	5	0	0	−1/2

A27. An orbital with the quantum numbers $n = 4$, $l = 3$, $m_l = 0$ and $m_s = -\frac{1}{2}$ is

(a) 3s (b) 3p

(c) 4d (d) 4f

A28. Which of the following orbital designations is not correct corresponding to quantum numbers ?

(a) $n = 5, l = 2 \longrightarrow 5d$

(b) $n = 2, l = 0 \longrightarrow 2s$

(c) $n = 4, l = 3 \longrightarrow 4f$

(d) $n = 7, l = 2 \longrightarrow 7p$

A29. The orbital angular momentum for an electron revolving in an orbit for an s-electron is

(a) zero (b) $\frac{h}{2\pi}$

(c) $\sqrt{2}\frac{h}{2\pi}$ (d) $\frac{1}{2} \cdot \frac{h}{2\pi}$

A30. The following quantum numbers are possible for how many orbitals ?

$n = 3, l = 2, m_l = +2$

(a) 1 (b) 2

(c) 3 (d) 4

Answers

A13. (b)	**A14.** (d)	**A15.** (c)	**A16.** (d)	**A17.** (b)	**A18.** (d)	**A19.** (c)	**A20.** (a)	**A21.** (d)	
A22. (c)	**A23.** (d)	**A24.** (b)	**A25.** (a)	**A26.** (c)	**A27.** (d)	**A28.** (d)	**A29.** (a)	**A30.** (a)	

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Shapes of Orbitals and Electronic Configurations

A31. The correct ground state electronic configuration of chromium atom (Z = 24) is :
(a) [Ar] $3d^5\,4s^1$ (b) [Ar] $3d^4\,4s^2$
(c) [Ar] $3d^6\,4s^0$ (d) [Ar] $4s^1\,4p^5$.

A32. In manganese atom, Mn (Z = 25), the total number of orbitals populated by one or more electrons (in ground state) is :
(a) 15 (b) 14
(c) 12 (d) 10.

A33. Which of the following has maximum number of unpaired electrons ?
(a) Mg^{2+} (b) Ti^{3+}
(c) V^{3+} (d) Fe^{3+}.

A34. Azimuthal quantum number for the last electron in Na atom is :
(a) 1 (b) 0
(c) 2 (d) 3.

A35. Orbital angular momentum depends on
(a) l (b) n and l
(c) n and m (d) m and s

A36. How many electrons in Argon have $m = 0$?
(a) 12 (b) 10
(c) 8 (d) 6.

A37. Magnetic quantum number for the valence electron of potassium is :
(a) 0 (b) 1
(c) 2 (d) 7.

A38. Consider the following ions :
1. Ni^{2+} **2.** Co^{2+} **3.** Cr^{2+} **4.** Fe^{3+}
(Atomic number : Cr = 24, Fe = 26, Co = 27 and Ni = 28)
The correct sequence of increasing number of unpaired electrons in these ions is
(a) 1, 2, 3, 4 (b) 4, 2, 3, 1.
(c) 1, 3, 2, 4 (d) 3, 4, 2, 1

A39. If the value of $(n + l)$ is more than 3 and less than 6, what will be the possible number of orbitals
(a) 6 (b) 9
(c) 10 (d) 13

A40. In an atom, the signs of lobes indicate the
(a) sign of charges
(b) sign of probability distribution
(c) sign of wave function
(d) presence or absence of electron

A41. The number of radial nodes possible for 3*d* orbital is
(a) 3 (b) 1
(c) 2 (d) 0

A42. The radial part of wave function depends on the quantum numbers
(a) n, l (b) n only
(c) l, m_l (d) l only

A43. The number of radial and angular nodes in 3*p* orbital are
(a) 1, 0 (b) 2, 1
(c) 1, 1 (d) 2, 0

A44. Consider the ground state of Cr atom (Z = 24). The number of electrons with azimuthal quantum numbers $l = 1$ and 2 are respectively
(a) 16 and 4 (b) 12 and 5
(c) 12 and 4 (d) 16 and 5

A45. Which of the following 3*d*-orbital has electron density in all the three axes?
(a) $3d_{xy}$ (b) $3d_{x^2-y^2}$
(c) $3d_{z^2}$ (d) $3d_{yz}$

A46. How many spherical nodes are present in 4*s* orbital in a hydrogen atom?
(a) 0 (b) 2
(c) 3 (d) 4

Answers

A31. (a) **A32.** (a) **A33.** (d) **A34.** (b) **A35.** (a) **A36.** (b) **A37.** (a) **A38.** (a) **A39.** (d) **A40.** (c)
A41. (d) **A42.** (a) **A43.** (c) **A44.** (b) **A45.** (c) **A46.** (c)

B MULTIPLE CHOICE QUESTIONS *from competitive examinations*

AIPMT & Other State Boards' Medical Entrance

B1. The de-Broglie wavelength associated with a ball of mass 1 kg having kinetic energy 0.5 J is
(a) 6.626×10^{-34} m (b) 13.20×10^{-34} m
(c) 10.38×10^{-21} m (d) 6.626×10^{-34} Å
(A.I.I.M.S. 2006)

B2. Consider the following sets of quantum numbers :

	n	l	m	s
(A)	3	0	0	+1/2
(B)	2	2	1	+1/2
(C)	4	3	–2	–1/2
(D)	1	0	–1	–1/2
(E)	3	2	3	+1/2

Which of the following sets of quantum numbers is not possible ?
(a) A, B, C and D (b) B, D and E
(c) A and C (d) B, C and D
(C.B.S.E. Med. 2007)

Answers

B1. (a) **B2.** (b)

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B3. The maximum kinetic energy of photoelectrons ejected from a metal, when it is irradiated with radiation of frequency $2 \times 10^{14}\ s^{-1}$ is 6.63×10^{-20} J. The threshold frequency of the metal is

(a) $2 \times 10^{14}\ s^{-1}$ (b) $3 \times 10^{14} s^{-1}$

(c) $2 \times 10^{-14}\ s^{-1}$ (d) $1 \times 10^{-14}\ s^{-1}$

(e) $1 \times 10^{14}\ s^{-1}$ *(Kerala P.M.T. 2008)*

B4. If uncertainty in position and momentum are equal, then uncertainty in velocity is

(a) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$ (b) $\sqrt{\frac{h}{2\pi}}$

(c) $\frac{1}{m}\sqrt{\frac{h}{\pi}}$ (d) $\sqrt{\frac{h}{\pi}}$

(C.B.S.E. P.M.T. 2008)

B5. The measurement of the electron position is associated with an uncertainty in momentum which is equal to 1×10^{-18} g cm s^{-1}. The uncertainty in velocity of electron (mass of electron is 9×10^{-28}g) is

(a) 1×10^{9} cm s^{-1} (b) 1×10^{6} cm s^{-1}

(c) 1×10^{5} cm s^{-1} (d) 1×10^{11} cm s^{-1}

(C.B.S.E.P.M.T. 2008)

B6. The velocity of particle A is 0.1 m/s and that of particle B is 0.05 m/s. If the mass of particle B is five times that of particle A, then the ratio of de-Broglie wavelength associated with particles A and B is

(a) 2 : 5 (b) 3 : 4

(c) 6 : 4 (d) 4 : 3

(e) 5 : 2 *(Kerala PMT 2009)*

B7. Maximum number of electrons in a subshell of an atom is determined by the following :

(a) $2l + 1$ (b) $4l - 2$

(c) $2n^2$ (d) $4l + 2$

(C.B.S.E. PMT 2009)

B8. Which of the following is not permissible arrangement of electrons in an atom ?

(a) $n = 5\ \ l = 3\ \ m = 0\ \ s = +1/2$

(b) $n = 3\ \ l = 2\ \ m = -3\ \ s = -1/2$

(c) $n = 3\ \ l = 2\ \ m = -2\ \ s = -1/2$

(d) $n = 4\ \ l = 0\ \ m = 0\ \ s = -1/2$

(C.B.S.E. PMT 2009)

B9. Which one of the following ion has electronic configuration [Ar] $3d^6$?

(a) Fe^{3+} (b) Co^{3+}

(c) Ni^{3+} (d) Mn^{3+}

(C.B.S.E. Med. 2010)

B10. The total number of atomic orbitals in fourth energy level of an atom is

(a) 8 (b) 16

(c) 32 (d) 4 *(AIPMT 2011)*

B11. The energies E_1 and E_2 of two radiations are 25 eV and 50 eV respectively. The relation between their wavelengths i.e., λ_1 and λ_2 will be

(a) $\lambda_1 = \lambda_2$ (b) $\lambda_1 = 2\lambda_2$

(c) $\lambda_1 = 4\lambda_2$ (d) $\lambda_1 = \frac{1}{2}\lambda_2$ *(AIPMT 2011)*

B12. If $n = 6$, the correct sequence for filling of electrons will be

(a) $ns \rightarrow (n-2)f \rightarrow (n-1)d \rightarrow np$

(b) $ns \rightarrow (n-1)d \rightarrow (n-2)f \rightarrow np$

(c) $ns \rightarrow (n-2)f \rightarrow np \rightarrow (n-1)d$

(d) $ns \rightarrow np(n-1)d \rightarrow (n-2)f$ *(AIPMT 2011)*

B13. Maximum number of electrons in a subshell with $\ell = 3$ and $n = 4$ is

(a) 14 (b) 16 (c) 10 (d) 12

(A.I.P.M.T. 2012)

B14. The correct set of four quantum numbers for the valence electron of rubidium atom (Z = 37) is

(a) 5, 1, 1 + 1/2 (b) 6, 0, 0, + 1/2

(c) 5, 0, 0, + 1/2 (d) 5, 1, 0, + 1/2

(A.I.P.M.T. 2012)

B15. What is the maximum number of electrons that can be associated with the following set of quantum numbers ?

$n = 3, l = 1$ and $m = -1$

(a) 4 (b) 2

(c) 10 (d) 6 *(NEET 2013)*

B16. Based on equation $E = -2.178 \times 10^{-18}\ J \left(\frac{Z^2}{n^2}\right)$, certain conclusions are written. Which of them is not correct ?

(a) Equation can be used to calculate the change in energy when the electron changes orbit.

(b) For $n = 1$, the electron has a more negative energy than it does for $n = 6$ which means that the electron is more loosely bound in the smallest allowed orbit.

(c) The negative sign in equation simply means that the energy of electron bound to the nucleus is lower than it would be if the electrons were at the infinite distance from the nucleus.

(d) Larger the value of n, the larger is the orbit radius.

(NEET 2013)

B17. The value of Planck's constant is 6.63×10^{-34} J s. The speed of light is 3×10^{17} nm s^{-1}. Which value is closest to the wavelength in nanometer of a quantum of light with frequency of $6 \times 10^{15}\ s^{-1}$?

(a) 50 (b) 75

(c) 10 (d) 25 *(NEET 2013)*

Answers

B3. (e) **B4.** (a) **B5.** (a) **B6.** (e) **B7.** (d) **B8.** (b) **B9.** (b) **B10.** (b) **B11.** (b) **B12.** (a)
B13. (a) **B14.** (c) **B15.** (b) **B16.** (b) **B17.** (a)

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B18. The ratio of de Broglie wavelengths of a deuterium atom to that of an α-particle, when the velocity of the former is five times greater than that of the latter, is
(a) 4 (b) 0.2
(c) 2 (d) 0.4
(e) 5 *(Kerala PMT 2014)*

B19. The uncertainty in the velocity of a particle of mass 6.626×10^{-31} kg is 1×10^{6} m s^{-1}. What is the uncertainty in its position (in nm)? ($h = 6.626 \times 10^{-34}$ J s)
(a) $\left(\frac{1}{2\pi}\right)$ (b) $\left(\frac{2.5}{\pi}\right)$
(c) $\left(\frac{4}{\pi}\right)$ (d) $\left(\frac{1}{4\pi}\right)$
(e) $\left(\frac{5}{\pi}\right)$ *(Kerala PMT 2014)*

B20. What is the maximum number of orbitals that can be identified with the following quantum numbers?
$n = 3, l = 1, m_l = 0$
(a) 1 (b) 2
(c) 3 (d) 4 *(AIPMT 2014)*

B21. Calculate the energy in joule corresponding to light of wavelength 45 nm.
(Planck's constant, $h = 6.63 \times 10^{-34}$ Js, speed of light, $c = 3 \times 10^{8}$ ms^{-1})
(a) 6.67×10^{15} (b) 6.67×10^{11}
(c) 4.42×10^{-15} (d) 4.42×10^{-18}
(AIPMT 2014)

B22. Magnetic moment 2.83 BM is given by which of the following ions?
(At. nos. Ti = 22, Cr = 24, Mn = 25, Ni = 28)
(a) Ti^{3+} (b) Ni^{2+}
(c) Cr^{3+} (d) Mn^{2+} *(AIPMT 2014)*

B23. Which one of the following sets of quantum numbers is possible?
(a) $n = 3, l = 3, m_l = -3, m_s = +1/2$
(b) $n = 2, l = 1, m_l = 2, m_s = -1/2$
(c) $n = 2, l = 0, m_l = 0, m_s = +1/2$
(d) $n = 1, l = 0, m_l = 0, m_s = 0$
(e) $n = 3, l = 2, m_l = 3, m_s = -1/2$
(Kerala PMT 2015)

B24. The angular momentum of electron in 'd' orbital is equal to ?
(a) $2\sqrt{3}\,\hbar$ (b) $0\,\hbar$
(c) $\sqrt{6}\,\hbar$ (d) $\sqrt{2}\,\hbar$ *(AIPMT 2015)*

B25. Which is the correct order of increasing energy of the listed orbitals in the atom of titanium ?
(At. no. Z = 22)
(a) 3*s* 3*p* 3*d* 4*s* (b) 3*s* 3*p* 4*s* 3*d*
(c) 3*s* 4*s* 3*p* 3*d* (d) 4*s* 3*s* 3*p* 3*d*
(AIPMT 2015)

B26. The number of d–electrons in Fe^{2+} (Z = 26) is not equal to the number of electrons in which one of the following?
(a) *d*-electrons in Fe (Z = 26)
(b) *p*-electrons in Ne (Z = 10)
(c) *s*-electrons in Mg (Z = 12)
(d) *p*-electrons in Cl (Z = 17) *(AIPMT 2015)*

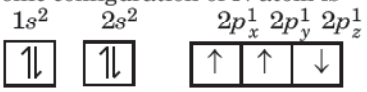
B27. The electrons occupying the same orbital are distinguished by
(a) azimuthal quantum number
(b) spin quantum number
(c) principal quantum number
(d) magnetic quantum number *(NEET 2016)*

B28. How many electrons can fit in the orbital for which $n = 3$ and $l = 1$?
(a) 2 (b) 6
(c) 10 (d) 14 *(NEET 2016)*

B29. Which of the following pairs of *d*-orbitals will have electron density along the axes?
(a) d_{z^2}, d_{xz} (b) d_{xz}, d_{yz}
(c) $d_{z^2}, d_{x^2-y^2}$ (d) $d_{zy}, d_{x^2-y^2}$ *(NEET2016)*

B30. Which one is the wrong statement?
(a) The uncertainty principle is $\Delta x \times \Delta v \geq \frac{h}{4\pi}$
(b) Half-filled and fully-filled orbitals have greater stability due to greater exchange energy, greater symmetry and more balanced arrangement.
(c) The energy of 2*s*-orbital is less than the energy of 2*p*-orbital in case of hydrogen like atoms.
(d) de-Broglie's wavelength is given by $\lambda = \frac{h}{mv}$, where
m = mass of the particle, v = velocity of the particle
(NEET 2017)

B31. Which one is a wrong statement?
(a) Total orbital angular momentum of electron in *s*-orbital is equal to zero.
(b) An orbital is designated by three quantum numbers while an electron in an atom is designated by four quantum numbers.
(c) The electronic configuration of N atom is



(d) The value of m for d_{z^2} is zero. *(NEET 2018)*

Answers

B18. (d) **B19.** (d) **B20.** (a) **B21.** (d) **B22.** (b) **B23.** (c) **B24.** (c) **B25.** (a) **B26.** (d) **B27.** (b)
B28. (a) **B29.** (c) **B30.** (c) **B31.** (c)

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JEE (Main) & Other State Boards' Engineering Entrance

B32. In a multielectron atom, which of the following orbitals described by the three quantum numbers will have the same energy in the absence of magnetic and electric fields ?

(*i*) $n = 1, l = 0, m = 0$ (*ii*) $n = 2, l = 0, m = 0$

(*iii*) $n = 2, l = 1, m = 1$ (*iv*) $n = 3, l = 2, m = 1$

(*v*) $n = 3, l = 2, m = 0$

(*a*) (*i*) and (*ii*) (*b*) (*ii*) and (*iii*)

(*c*) (*iii*) and (*iv*) (*d*) (*iv*) and (*v*)

(A.I.E..E.E. 2005)

B33. According to Bohr's theory, the angular momentum of an electron in 5th orbit is

(*a*) $1.0\,h/\pi$ (*b*) $10\,h/\pi$

(*c*) $2.5\,h/\pi$ (*d*) $25\,h/\pi$

(A.I.E.E.E. 2006)

B34. Uncertainty in the position of an electron (mass = 9.1×10^{-31} kg) moving with a velocity 300 ms^{-1}, accurate upto 0.001% will be

(*a*) 5.76×10^{-2} m (*b*) 1.92×10^{-2} m

(*c*) 3.84×10^{-2} m (*d*) 19.2×10^{-2} m

(*e*) $= 6.63 \times 10^{-34}$ Js) *(A.I.E.E.E. 2006)*

B35. The radius of the first Bohr orbit of hydrogen atom is 0.59 Å. The radius of third orbit of He^+ will be

(*a*) 8.46 Å (*b*) 0.705 Å

(*c*) 1.59 Å (*d*) 1.41 Å

(*e*) 2.38 Å *(Kerala C.E.T. 2007)*

B36. Which of the following sets of quantum numbers represents the highest energy of an atom ?

(*a*) $n = 3, l = 2, m = 1, s = +1/2$

(*b*) $n = 4, l = 0, m = 0, s = +1/2$

(*c*) $n = 3, l = 0, m = 0, s = +1/2$

(*d*) $n = 3, l = 1, m = 1, s = +1/2$ *(A.I.E.E.E. 2007)*

B37. The ionization enthalpy of hydrogen atom is 1.312×10^6 $J\,mol^{-1}$. The energy required to excite the electron in the atom from $n = 1$ to $n = 2$ is

(*a*) 9.84×10^5 J mol^{-1} (*b*) 8.51×10^5 J mol^{-1}

(*c*) 6.56×10^5 J mol^{-1} (*d*) 7.56×10^5 J mol^{-1}

(A.I.E.E.E. 2008)

B38. In an atom, an electron is moving with a speed of 600 m/s with an accuracy of 0.005%. Certainty with which the position of an electron can be located is ($h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}; mass of electron, $e_m = 9.1 \times 10^{-31}$ kg)

(*a*) 1.52×10^{-4} m (*b*) 5.10×10^{-3} m

(*c*) 1.92×10^{-3} m (*d*) 3.84×10^{-3} m

(A.I.E.E.E. 2009)

B39. Calculate the wavelength associated with a proton moving at 1.0×10^3 m/s. (Mass of proton = 1.67×10^{-27} kg and $h = 6.63 \times 10^{-34}$ Js)

(*a*) 0.032 nm (*b*) 0.40 nm

(*c*) 2.5 nm (*d*) 14.0 nm

(A.I.E.E.E. 2009)

B40. What is the maximum number of emission lines obtained when the excited electrons of a hydrogen atom in $n = 5$ drop to ground state ?

(*a*) 10 (*b*) 5

(*c*) 12 (*d*) 15 *(J.K. CET 2010)*

B41. The wave number of the spectral line in the emission spectrum of hydrogen will be equal to $\frac{8}{9}$ times the Rydberg's constant if the electron jumps from

(*a*) $n = 3$ to $n = 1$ (*b*) $n = 10$ to $n = 1$

(*c*) $n = 9$ to $n = 1$ (*d*) $n = 2$ to $n = 1$

(Karnataka CET 2010)

B42. The shortest wavelength in hydrogen spectrum of Lyman series when $R_H = 109678$ cm^{-1} is

(*a*) 1002.7Å (*b*) 1215.67Å

(*c*) 1127.30Å (*d*) 911.7Å

(*e*) 1234.7Å *(Kerala PET 2010)*

B43. Ionisation energy of He^+ is 19.6×10^{-18} J $atom^{-1}$. The energy of first stationary state (n =1) of Li^{2+} is

(*a*) $-2.2. \times 10^{-15}$ J $atom^{-1}$

(*b*) 8.82×10^{-17} J $atom^{-1}$

(*c*) 4.41×10^{-16} J $atom^{-1}$

(*d*) -4.41×10^{-17} J $atom^{-1}$ *(A.I.E.E.E. 2010)*

B44. Which transition in the hydrogen atomic spectrum will have the same wavelength as the transition, $n = 4$ to $n = 2$ of He^+ spectrum ?

(*a*) $n = 4$ to $n = 3$ (*b*) $n = 3$ to $n = 2$

(*c*) $n = 4$ to $n = 2$ (*d*) $n = 3$ to $n = 1$

(*e*) $n = 2$ to $n = 1$ *(Kerala PET 2011)*

B45. For Balmer series in the spectrum of atomic hydrogen, the wave number of each lines is given by $\bar{\nu} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ where R_H is a constant and n_1 and n_2 are integers. Which of the following statement(*s*) is (are) correct?

1. As wavelength decreases, the lines in the series converage.
2. The integer n_1 is equal to 2
3. The ionization energy of hydrogen can be calculated from the wave number of these lines
4. The line of longest wavelegnth corresponds to $n_2 = 3$.

(*a*) 1, 2 and 3 (*b*) 2, 3 and 4

(*c*) 1, 2 and 4 (*d*) 2 and 4 only

(*e*) 2 only *(Kerala PET 2011)*

Answers

B32. (*d*) **B33.** (*c*) **B34.** (*b*) **B35.** (*e*) **B36.** (*a*) **B37.** (*a*) **B38.** (*c*) **B39.** (*b*) **B40.** (*a*) **B41.** (*a*) **B42.** (*d*) **B43.** (*d*) **B44.** (*e*) **B45.** (*c*)

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B46. The frequency of light emitted for the transition $n = 4$ to $n = 2$ of He^+ is equal to the transition in H-atom corresponding to which of following ?

(*a*) $n = 2$ to $n = 1$ (*b*) $n = 3$ to $n = 2$

(*c*) $n = 4$ to $n = 3$ (*d*) $n = 3$ to $n = 1$

(AIEEE 2011)

B47. The ratio of the frequency corresponding to the third line in Lyman series of hydrogen atomic spectrum to that of the first line in Balmer series of Li^{2+} spectrum is

(*a*) $\frac{4}{5}$ (*b*) $\frac{5}{4}$

(*c*) $\frac{4}{3}$ (*d*) $\frac{3}{4}$

(*e*) $\frac{3}{8}$ *(Kerala P.E.T. 2012)*

B48. The correct set of four quantum numbers for the outermost electron of sodium (Z = 11) is

(*a*) $3, 1, 0, \frac{1}{2}$ (*b*) $3, 1, 1, \frac{1}{2}$

(*c*) $3, 2, 1, \frac{1}{2}$ (*d*) $3, 0, 0, \frac{1}{2}$

(Karnataka C.E.T. 2012)

B49. The electrons identified by quantum numbers n and ℓ :

(1) $n = 4, \ell = 1$ (2) $n = 4, \ell = 0$

(3) $n = 3, \ell = 2$ (4) $n = 3, \ell = 1$

can be placed in order of increasing energy as

(*a*) (4) < (2) < (3) < (1) (*b*) (2) < (4) < (1) < (3)

(*c*) (1) < (3) < (2) < (4) (*d*) (3) < (4) < (2) < (1)

(A.I. E.E.E. 2012)

B50. The electronic configuration of Cu^{2+} ion is

(*a*) [Ar] $3d^8 4s^1$ (*b*) [Ar] $3d^9 4s^0$

(*c*) [Ar] $3d^7 4s^2$ (*d*) [Ar] $3d^8 4s^0$

(Karnataka CET 2013)

B51. The ionization enthalpy of He^+ ion is 19.60×10^{-18} J atom^{-1}. The ionization enthalpy of Li^{2+} ion will be

(*a*) 84.2×10^{-18} J atom^{-1}

(*b*) 44.10×10^{-18} J atom^{-1}

(*c*) 63.20×10^{-18} J atom^{-1}

(*d*) 21.20×10^{-18} J atom^{-1}

(*e*) 2.17×10^{-19} J atom^{-1} *(Kerala P.E.T. 2013)*

B52. The orbital diagram in which Aufbau principle is violated is

(*a*) ↿⇂ ↿⇂ 1 _ (*b*) ↿⇂ 1 1 1

(*c*) 1 ↿⇂ 1 1 (*d*) ↿⇂ ↿⇂ 1 1

(JK CET 2013)

B53. Energy of an electron is given by

$E = -2.178 \times 10^{-18}\ J \left(\frac{Z^2}{n^2}\right)$. Wavelength of light required to excite an electron in a hydrogen atom from level $n = 1$ to $n = 2$ will be ($h = 6.62 \times 10^{-34}$ J s and $c = 3.0 \times 10^8$ m s^{-1})

(*a*) 8.500×10^{-7} m (*b*) 1.214×10^{-7} m

(*c*) 2.816×10^{-7} m (*d*) 6.500×10^{-7} m

(JEE Main 2013)

B54. As per de Broglie's formula, a macroscopic particle of mass 100 g and moving at a velocity of 100 cm s^{-1} will have a wavelength of

(*a*) 6.6×10^{-29} cm (*b*) 6.6×10^{-30} cm

(*c*) 6.6×10^{-31} cm (*d*) 6.6×10^{-32} cm

(WB JEE 2014)

B55. The shortest wavelength of the line in hydrogen atomic spectrum of Lyman series when $R_H = 109678$ cm^{-1} is

(*a*) 1002.7 Å (*b*) 1215.67 Å

(*c*) 1127.30 Å (*d*) 911.7 Å

(*e*) 1234.7 Å *(Kerala PET 2014)*

B56. The correct set of four quantum numbers for the valence electrons of rubidium atom (Z = 37) is

(*a*) $5, 0, 1, +\frac{1}{2}$ (*b*) $5, 0, 0, +\frac{1}{2}$

(*c*) $5, 1, 0, +\frac{1}{2}$ (*d*) $5, 1, 1, +\frac{1}{2}$

(JEE Main 2014)

B57. Which of the following is the energy of a possible excited state of hydrogen?

(*a*) –3.4 eV (*b*) + 6.8 eV

(*c*) + 13.6 eV (*d*) –6.8 eV

(JEE Main 2015)

B58. The time taken for an electron to complete one revolution in Bohr orbit of hydrogen atom is

(*a*) $\frac{4m^2\pi r^2}{n^2h^2}$ (*b*) $\frac{n^2h^2}{4mr^2}$

(*c*) $\frac{4\pi^2mr^2}{nh}$ (*d*) $\frac{nh}{4\pi^2mr^2}$

(WB JEE 2016)

B59. In the hydrogen atomic spectrum, the emission of the least energetic photon takes place during the transition from n = 6 energy level to n = ... energy level.

(*a*) 1 (*b*) 3

(*c*) 5 (*d*) 4

(*e*) 2 *(Kerala PET 2016)*

Answers

B46. (*a*) **B47.** (*d*) **B48.** (*d*) **B49.** (*a*) **B50.** (*b*) **B51.** (*b*) **B52.** (*c*) **B53.** (*b*) **B54.** (*c*) **B55.** (*d*)
B56. (*b*) **B57.** (*a*) **B58.** (*c*) **B59.** (*c*)

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B60. The energy of electron in the nth Bohr orbit of H-atom is

(a) $\frac{-13.6}{n^2}$eV (b) $\frac{-13.6}{n}$eV

(c) $\frac{-13.6}{n^4}$eV (d) $\frac{-13.6}{n^3}$eV

(Karnataka C.E.T. 2016)

B61. Consider the following sets of quantum numbers. Which of the below setting is not permissible arrangement of electrons in an atom?

	n	l	m	s
(a)	4	0	0	$-\frac{1}{2}$
(b)	5	3	0	$+\frac{1}{2}$
(c)	3	2	–2	$-\frac{1}{2}$
(d)	3	2	–3	$+\frac{1}{2}$

(Kerala PET 2016)

B62. A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference V e.s.u. If e and m are charge and mass of an electron respectively, then the value of h/λ (where λ is wavelength associated with electron wave) is given by

(a) meV (b) 2meV

(c) $\sqrt{meV}$ (d) $\sqrt{2meV}$

(JEE Main 2016)

B63. If the given four electronic configurations

(a) $n = 4, l = 1$ (b) $n = 4, l = 0$

(c) $n = 3, l = 2$ (d) $n = 3, l = 1$

are arranged in order of increasing energy, then the order will be

(a) *(iv) < (ii) < (iii) < (i)*

(b) *(ii) < (iv) < (i) < (iii)*

(c) *(i) < (iii) < (ii) < (iv)*

(d) *(iii) < (i) < (iv) < (ii)* *(WB JEE 2017)*

B64. Which of the following set of quantum numbers represents the 19th electron of Cr (Z = 24)?

(a) $(4, 1, -1, +\frac{1}{2})$ (b) $(4, 0, 0, +\frac{1}{2})$

(c) $(3, 2, 0, -\frac{1}{2})$ (d) $(3, 2, -2, +\frac{1}{2})$

(WB JEE 2017)

B65. The correct set of quantum numbers for the unpaired electron of chlorine atom is

(a) $2, 0, 0, +\frac{1}{2}$ (b) $3, 0, 0, \pm\frac{1}{2}$

(c) $2, 1, -1, +\frac{1}{2}$ (d) $3, 1, 1, \pm\frac{1}{2}$

(Karnataka CET 2017)

B66. The energy of an electron in the 3*s* orbital (excited state) of H-atom is

(a) – 1.5 eV (b) – 13.6 eV

(c) – 3.4 eV (d) – 4.53 eV

(e) 4.53 eV *(Kerala PET 2017)*

B67. The radius of the second Bohr orbit for hydrogen atom is :

(Planck's constant, $h = 6.6262 \times 10^{-34}$Js; mass of electron = 9.1091×10^{-31} kg; charge of electron $e = 1.60210 \times 10^{-19}$ C; permittivity of vaccum $\epsilon_0 = 8.854185 \times 10^{-12}$ kg^{-1} m^{-3} A^2)

(a) 1.65 Å (b) 4.76 Å

(c) 0.529 Å (d) 2.12 Å

(JEE Main 2017)

B68. Which of the following set of quantum numbers is not possible?

(a) $n = 3, l = 0, m = 0$ (b) $n = 3, l = 1, m = -1$

(c) $n = 2, l = 0, m = -1$ (d) $n = 2, l = 1, m = 0$

(WB JEE 2018)

B69. The number of unpaired electrons in Ni (atomic number = 28) are

(a) 0 (b) 2

(c) 4 (d) 8 *(WB JEE 2018)*

B70. With respect to atomic spectrum, each line in the Lyman series is due to electrons returning

(a) from a particular higher energy level to $n = 3$

(b) from a particular higher energy level to $n = 2$

(c) from a particular higher energy level to $n = 1$

(d) from a particular higher energy level to $n = 4$

(J.K. CET 2018)

B71. The orbital nearest to the nucleus is

(a) 4*f* (b) 5*d*

(c) 4*s* (d) 7*p*

(Karnataka CET 2018)

B72. What is the work function of the metal if the light of wavelength 4000 Å generates photoelectrons of velocity 6×10^5 ms^{-1} from it?

(Mass of electron = 9×10^{-31} kg

Velocity of light = 3×10^8 ms^{-1}

Planck's constant = 6.626×10^{-34} Js

Charge of electron = 1.6×10^{-19} JeV^{-1})

(a) 4.0 eV (b) 2.1 eV

(c) 3.1 eV (d) 0.9 eV

(JEE Main 2019)

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B73. The radius of which of the following orbit is same as that of the first Bohr's orbit of hydrogen atom ?

(a) $He^+ (n = 2)$ (b) $Li^{2+} (n = 2)$

(c) $Li^{2+} (n = 3)$ (d) $Be^{3+} (n = 2)$

(I.I.T. 2004)

Answers

B60. (a) **B61.** (d) **B62.** (d) **B63.** (a) **B64.** (b) **B65.** (d) **B66.** (a) **B67.** (d) **B68.** (c) **B69.** (b)
B70. (c) **B71.** (c) **B72.** (b) **B73.** (d)

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B74. The number of radial nodes of 3*s* and 2*p*-orbitals are respectively :

(*a*) 2, 0 (*b*) 0, 2

(*c*) 1, 2 (*d*) 2, 1

(I.I.T. Screening 2005)

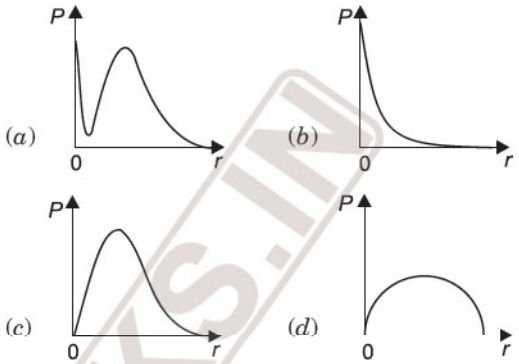
B75. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom [a_0 is Bohr radius]

(*a*) $\frac{h^2}{4\pi^2 m a_0^2}$ (*b*) $\frac{h^2}{16\pi^2 m a_0^2}$

(*c*) $\frac{h^2}{32\pi^2 m a_0^2}$ (*d*) $\frac{h^2}{64\pi^2 m a_0^2}$

(I.I.T. J.E.E. 2012)

B76. P is the probability of finding the 1*s* electron of hydrogen atom in a spherical shell of infinitesimal thickness *dr*, at a distance *r* from the nucleus. The volume of this shell is $4\pi r^2 dr$. The qualitative sketch of the dependence of P on *r* is?



(JEE Advance 2016)

Answers

B74. (*a*) **B75.** (*c*) **B76.** (*c*)

C MULTIPLE CHOICE QUESTIONS
with more than one correct answer

C1. Which of the following statements are correct ?

(*a*) Radial wave function gives the shape of the orbital

(*b*) Radial wave function depends upon *n* and *l*.

(*c*) 3*p* orbital has two spherical nodes

(*d*) 3*d* orbital has no spherical node

C2. Which of the following are correct notations for the orbitals ?

(*a*) $n = 3, l = 2 \longrightarrow 3d$

(*b*) $n = 4, l = 1 \longrightarrow 4p$

(*c*) $n = 4, l = 3 \longrightarrow 4d$

(*d*) $n = 6, l = 1 \longrightarrow 6f$

C3. The orbitals having the same number of spherical nodes are :

(*a*) 4*p*, 3*d* (*b*) 3*p*, 4*d*

(*c*) 4*s*, 5*p* (*d*) 2*s*, 3*d*

C4. Which of the following set of ions have the same number of electrons ?

(*a*) Cr^{3+}, Fe^{2+} (*b*) Cu^{+}, Zn^{2+}

(*c*) Mn^{2+}, Fe^{3+} (*d*) Sc^{3+}, V^{3+}

C5. Which of the following species are isoelectronic ?

(*a*) O^{2-} (*b*) K^{+} (*c*) Na^{+} (*d*) N

C6. Which of the following atoms have same number of unpaired electrons ?

(*a*) Copper (Z = 29)

(*b*) Scandium (Z = 21)

(*c*) Manganese (Z = 25)

(*d*) Chromium (Z = 24)

C7. In which of the following the first orbital has higher energy than the second in H-atom ?

(*a*) $n = 4, l = 3$ and $n = 5, l = 0$

(*b*) $n = 3, l = 2$ and $n = 3, l = 1$

(*c*) $n = 3, l = 1$ and $n = 3, l = 2$

(*d*) $n = 3, l = 2$ and $n = 2, l = 1$ *(J.K. C.E.T. 2006)*

C8. Identify the correct statement(s).

The findings from the Bohr model for H-atom are

(*a*) angular momentum of the electron is expressed as integral multiples of $\frac{h}{2\pi}$

(*b*) the first Bohr radius is 0.529 Å

(*c*) the energy of the n^{th} level, E_n is proportional to $\frac{1}{n^2}$

(*d*) the spacing between adjacent levels increases with increase in '*n*' *(WB JEE 2017)*

Answers

C1. (*b*, *d*) **C2.** (*a*, *b*) **C3.** (*b*, *c*) **C4.** (*b*, *c*) **C5.** (*a*, *c*) **C6.** (*a*, *b*) **C7.** (*a*, *d*) **C8.** (*a*, *b*, *c*)

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D MULTIPLE CHOICE QUESTIONS
based on the given passage/comprehension

Passage I.

In 1924, de-Broglie proposed that every particle possesses wave properties with a wavelength, λ given by $\lambda = \frac{h}{mv}$ where m is the mass of the particle, v is its velocity and h is Planck's constant. The de-Broglie prediction was confirmed experimentally when it was found that an electron beam undergoes diffraction, a phenomenon characteristic of waves. The de-Broglie wavelength can be estimated by measuring kinetic energy of an electron accelerating by a potential V as :

$\frac{1}{2}mv^2 = eV$ where $1\ eV = 1.6 \times 10^{-19} C$, $h = 6.6 \times 10^{-34}$ J.

Answer the following questions :

D1. The mass of a photon moving with velocity of light having wavelength same as that of an α-particle (mass = 6.6×10^{-27} kg) moving with velocity of 2.5×10^2 ms^{-1} is

(a) 7.92×10^{-21} kg

(b) 5.5×10^{-33} kg

(c) 5.65×10^{-31} kg

(d) 7.92×10^{-28} kg

D2. The wavelength of matter wave associated with an electron passing through an electric potential of 100 million volts is

(a) $10^4 (2\,me)^{1/2} h$ (b) $\frac{h \times 10^{-4}}{(2\,me)^{1/2}}$

(c) $\frac{10^{-3} h}{(2\,me)^{1/2}}$ (d) $\frac{h \times 10^4}{(2\,me)^{-1/2}}$

D3. The proton and He^{2+} are accelerated by the same potential, then their de-Broglie wavelengths $\lambda_{He^{2+}}$ and λ_p are in the ratio of ($m_{He^{2+}} = 4m_p$) :

(a) $\frac{1}{\sqrt{2}}$ (b) $\frac{1}{2\sqrt{2}}$

(c) $2\sqrt{2}$ (d) $\frac{1}{2}$

D4. If λ is the wavelength associated with the electron in the 4th circular orbit of hydrogen atom, then radius of the orbit is

(a) $\frac{\lambda}{2\pi}$ (b) $\frac{\lambda}{\pi}$

(c) $\frac{2}{\pi\lambda}$ (d) $\frac{2\pi}{\lambda}$

D5. The wavelength of particles constituting a beam of helium atoms moving with a velocity of 2.0×10^4 ms^{-1} is

(a) 4.99 pm (b) 49.9 pm

(c) 499 nm (d) 499 pm

Passage II.

The position and energy of an electron is specified with the help of four quantum numbers namely, principal quantum number (n), azimuthal quantum number (l), magnetic quantum number (m_l) and spin quantum number (m_s). The permissible values of these are :

$n = 1, 2$

$n = 0, 1, ...(n-1)$

$m_1 = -l ..... 0, ... +l$

$m_s = +\frac{1}{2}$ and $-\frac{1}{2}$ for each value of m_l.

The angular momentum of electron is given as $\sqrt{l(l+1)}.\frac{h}{2\pi}$

While spin angular momentum is given as $\sqrt{s(s+1)}.\frac{h}{2\pi}$ where $s = \frac{1}{2}$

The electrons having the same value of n, l and m_l are said to belong to the same orbital. According to Pauli's exclusion principle, an orbital can have maximum of two electrons and these two must have opposite spin.

Answer the following questions :

D6. For an electron having $n = 3$ and $l = 0$, the orbital angular momentum is

(a) $\frac{\sqrt{3}\,h}{\pi}$ (b) $\sqrt{6}\,\frac{h}{2\pi}$

(c) zero (d) $2\sqrt{3}\,\frac{h}{\pi}$

D7. The maximum number of electrons having $n + l = 5$ in an atom is

(a) 32 (b) 18

(c) 10 (d) 8

D8. Which of the following statements is not correct ?

(a) For sodium, the outermost electron has $n = 3$, $l = 0$, $m_l = 0$, $s = +1/2$

(b) The orbitals having $n = 3$, $l = 2$, $m_l = +2$ and $n = 3$, $l = 2$, $m_l = -2$ have same energies.

(c) For 4f electron, $n = 4$, $l = 3$, $m_l = 0$, $s = +1/2$ is not possible.

(d) The orbitals 2d, 3f and 4g are not possible.

Answers

Passage I. **D1.** (b) **D2.** (b) **D3.** (d) **D4.** (c) **D5.** (a) **Passage II.** **D6.** (c) **D7.** (b) **D8.** (c)

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Passage III.

The hydrogen like species Li^{2+} is in a spherically symmetrical state S_1 with one radial node. Upon absorbing light the ion undergoes transition to a state S_2. The state S_2 has one radial node and its energy is equal to the ground state of the hydrogen atom.

Answer the following questions :

D9. The state S_1 is

(a) 1s (b) 2s
(c) 2p (d) 3s

D10. Energy of the state S_1 in units of the hydrogen atom ground state energy is

(a) 0.75
(b) 1.50
(c) 2.25
(d) 4.50

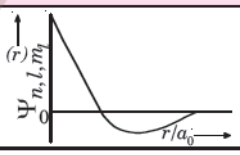
D11. The orbital angular momentum quantum number of the state S_2 is

(a) 0 (b) 1
(c) 2 (d) 3 *(I.I.T. 2010)*

Passage IV.

The wave function, $\psi_{n,\,l,\,m_l}$ is a mathematical function whose value depends upon spherical polar coordinates $(r, \theta, \phi,)$ of the electron and characterized by the quantum numbers n, l and m_l. Here r is distance from nucleus, θ is colatitude and ϕ is azimuth. In the mathematical functions given in the table, Z is atomic number and a_0 is Bohr radius.

Using this information which is available in three columns of the table, **answer the following questions:**

Column 1	Column 2	Column 3
(I) 1s orbital	(i) $\Psi_{n,l,m_l} \propto \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-(Zr/a_0)}$	(P) 
(II) 2s orbital	(ii) One radial node	(Q) Probability density at nucleus $\propto \frac{1}{a_0^3}$
(III) $2p_z$ orbital	(iii) $\psi_{n,\,l,\,m_l} \propto \left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\, e^{-\left(\frac{Zr}{2a_0}\right)} \cos\theta$	(R) Probability density is maximum at nucleus.
(IV) $3d_{z^2}$ orbital	(iv) xy-plane is a nodal plane	(S) Energy needed to excite electron from $n = 2$ state to $n = 4$ state is $\frac{27}{32}$ times the energy needed to excite electron from $n = 2$ state to $n = 6$ state

D12. For He^+ ion, the only incorrect combination is

(a) (I) (i) (R) (b) (II) (ii) (Q)
(c) (I) (i) (S) (d) (I) (iii) (R)

D13. For the given orbital in Column 1, the only correct combination for any hydrogen like species is

(a) (I) (ii) (S) (b) (IV) (iv) (R)
(c) (III) (iii) (P) (d) (II) (ii) (P)

D14. For hydrogen atom, the only correct combination is

(a) (II) (i) (Q)
(b) (I) (iv) (R)
(c) (I) (i) (P)
(d) (I) (i) (S)

(JEE Advance 2017)

Answers

Passage III. D9. (b) **D10.** (c) **D11.** (b) **Passage IV. D12.** (d) **D13.** (d) **D14.** (d)

Assertion Reason Type Questions

The questions given below consists of an Assertion and the Reason. Use the following key to choose the appropriate answer :

(a) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
(b) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.
(c) If assertion is CORRECT, but reason is INCORRECT.
(d) If assertion is INCORRECT, but reason is CORRECT.
(e) If both assertion and reason are INCORRECT.

1. Assertion : Hydrogen has one electron in its orbit but it produces several spectral lines.
Reason : There are many excited energy levles available. *(A.I.I.M.S. 1997)*

2. Assertion : The 19th electron in potassium atom enters into 4s-orbital and not in the 3d-orbital.

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Reason : $(n + l)$ rule is followed for determining the orbital of lowest energy state. *(A.I.I.M.S. 1999)*

3. **Assertion** : The energy of an electron is largely determined by its principal quantum number.
   Reason : The principal quantum number number (n) is a measure of the probable distance of finding the electron around the nucleus. *(A.I.I.M.S. 1998)*
4. **Assertion** : For the outermost electron in Na atom, the orbital angular momentum is zero.
   Reason : For 3*s* electron , $l = 0$ and orbital angular momentum is zero.
5. **Assertion** : The configuration of C cannot be $1s^2\,2s^2\,2p_x^2$.
   Reason : According to Pauli exclusion principle an orbital can have maximum of two electrons.
6. **Assertion** : 2*s*-orbital has two nodes.
   Reason : Number of nodes in an *s*- orbital is equal to *n* value.
7. **Assertion** : All microscopic bodies in motion have wave character.
   Reason : Microscopic bodies have very large mass.
8. **Assertion** : Cl^- ions and K^+ ions are isoelectronic.
   Reason : Isoelectronic ions have same charge.
9. **Assertion** : It is impossible to determine the exact position and exact momentum of an electron simultaneously.
   Reason : The path of an electron in an atom is clearly defined.
10. **Assertion** : Photoelectric effect is easily given by cesium metal.
    Reason : Photoelectric effect is easily given by the metals having high ionization enthalpy.
11. **Assertion** : Only principal quantum number determines the energy of an electron in an orbital of Na atom.
    Reason : For one electron system, the expression of energy is quite different from that obtained in Bohr's theory. *(AIIMS 2010)*

Answers

1. (*a*) **2.** (*a*) **3.** (*a*) **4.** (*a*) **5.** (*b*) **6.** (*e*) **7.** (*c*) **8.** (*c*) **9.** (*c*) **10.** (*c*) **11.** (*e*)

Matching List Type Questions

1. Match the orbital given in List-I with its description given in List-II and select the correct answer using the code given below the lists:

List-I	List-II
(P) $3p_z$	1. total number of nodes = 2
(Q) $4s$	2. has 3 radial nodes and 0 angular node
(R) $3d_{x^2-y^2}$	3. corresponds to $n = 3$, $l = 0$, $m_l = 0$
(S) $4p$	4.has no radial node

Code

	P	Q	R	S
(*a*)	2	4	3	1
(*b*)	4	2	3	1
(*c*)	4	1	3	2
(*d*)	3	2	4	1

2. Match the entries of List I with its discoverer given in List II and select the correct answer using the code given below the lists:

List I	List II
(P) discovery of proton	1. Chadwick
(Q) discovery of neutron	2. Goldstein
(R) determination of atomic number	3. Moseley
(S) determination of charge/ mass of electron	4. J.J. Thomson

Code

	P	Q	R	S
(*a*)	4	2	1	3
(*b*)	4	1	2	3
(*c*)	2	1	4	3
(*d*)	2	1	3	4

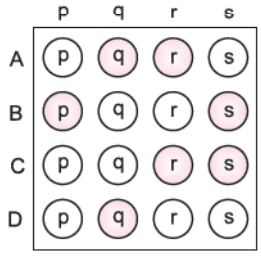
Answers

1. (*a*) **2.** (*d*)

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.

If the correct matches are A-*q*, A-*r*, B-*p*, B-*s*, C-*r*, C-*s* and D-*q*, then the correctly bubbled matrix will look like the following:



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1. Match the spectral series in Column I with its characteristics in Column II.

Column I	Column II
(A) Balmer series	(*p*) falls in infra red region
(B) Pfund series	(*q*) involve jumps from higher orbits to $n = 3$
(C) Brackett series	(*r*) falls in visible region
(D) Paschen series	(*s*) involve jumps from higher orbits to $n = 5$

2. Match the quantum number given in Column I with its description given in Column II

Column I	Column II
(A) n	(*p*) designates the orientation of orbital
(B) l	(*q*) orientation of the spin of the electron
(C) m_l	(*r*) has values corresponding to '*n*'
(D) m_s	(*s*) defines the shell

3. Match the entries in Column I with the correctly related quantum number(s) in ColumnII.

Column I	Column II
(A) Orbital angular momentum of the electron in a hydrogen-like atomic orbital.	(*p*) Principal quantum number
(B) A hydrogen-like one-electron wave function obeying Pauli principle	(*q*) Azimuthal quantum number
(C) Shape, size and orientation of hydrogen like atomic orbitals.	(*r*) Magnetic quantum number
(D) Probability density of electron at the nucleus in hydrogen-like atom.	(*s*) Electron spin quantum number

Answers

(1) : (A) – (*r*) (B) – (*p*), (*s*) (C) – (*p*) (D) – (*p*), (*q*) **(2)** : (A) – (*s*) (B) – (*r*) (C) – (*p*) (D) – (*q*)
(3) : (A)– (*q*) (B)– (*p*), (*q*), (*r*), (*s*) (C) – (*p*), (*q*) (*r*) (D) – (*p*), (*q*)

Integer Type and Numerical Value Type Questions

Integer Type: The answers to each of the following question is a single digit integer ranging from 0 to 9.

1. The maximum number of electrons that can have principal quantum number, $n = 3$ and spin quantum number, $m_s = +1/2$ is *(I.I.T. 2011)*

2. How many times is the ionization energy of He^+ ion as compared to that of H-atom?

3. Total number of orbitals in a *f*-sub-shell is

4. Number of unpaired electrons in Fe^{2+} ion is

5. The maximum number of electrons in an atom with $n = 4$ and $l = 1$ is

6. The value of angular momentum for an electron in 3*d* orbital is $\sqrt{x}\,\frac{h}{2\pi}$. The value of x is

7. Number of times radius of the 3rd shell of the H-atom as compared to that of radius of first shell is

8. The atomic masses of He and Ne are 4 and 20 a.m.u., respectively. The value of the de Broglie wavelength of He gas at –73°C is M times that of the de Broglie wavelength of Ne at 727°C. M is

(JEE Advanced 2013)

9. In an atom, the total number of electrons having quantum numbers, $n = 4$, $|m_l| = 1$ and $m_s = -1/2$ is

(JEE Advance 2014)

10. Not considering the electronic spin, the degeneracy of the second excited state ($n = 3$) of H atom is 9, while the degeneracy of the second excited state of H^- is *(JEE Advance 2015)*

Answers

1. (9) **2.** (4) **3.** (7) **4.** (4) **5.** (6) **6.** (6) **7.** (9) **8.** (5). **9.** (3). **10.** (3).

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NCERT Exemplar Problems

Multiple Choice Questions (Type-I)

Objective Questions

1. Which one of the following conclusions could not be derived from Rutherford's α-paticle scattering experiments ?

(*a*) Most of the space in the atom is empty.

(*b*) The radius of the atom is about 10^{-10} m while that of nucleus is 10^{-15} m.

(*c*) Electrons move in a circular path of fixed energy called orbits.

(*d*) Electrons and the nucleus are held together by electrostatic forces of attraction.

2. Which of the following options does not represent ground state electronic configuration of an atom ?

(*a*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$

(*b*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9\ 4s^2$

(*c*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

(*d*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

3. The probability density plots of 1*s* and 2*s* orbitals are given in Fig. 1 :

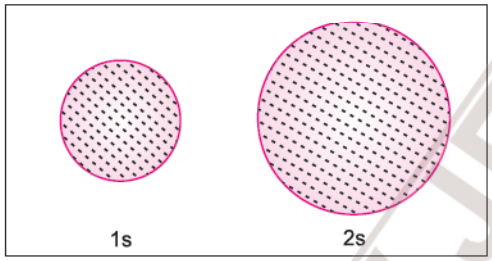

Fig. 1.

The density of dots in a region represents the probability density of finding electrons in the region.

On the basis of above diagram which of the following statements is incorrect ?

(*a*) 1*s* and 2*s* orbitals are spherical in shape.

(*b*) The probability of finding the electron is maximum near the nucleus.

(*c*) The probability of finding the electron at a given distance is equal in all directions.

(*d*) The probability density of electrons for 2*s* orbital decreases uniformly as distance from the nucleus increases.

4. Which of the following statements is **not** correct about the characteristics of cathode rays ?

(*a*) They start from the cathode and move towards the anode.

(*b*) They travel in straight line in the absence of an external electrical or magnetic field.

(*c*) Characteristics of cathode rays do not depend upon the material of electrodes in cathode ray tube.

(*d*) Characteristics of cathode rays depend upon the nature of gas present in the cathode ray tube.

5. Which of the following statement about the electron is incorrect ?

(*a*) It is a negatively charged particle

(*b*) The mass of electron is equal to the mass of neutron

(*c*) It is a basic constituent of all atoms

(*d*) It is a constituent of cathode rays

6. Which of the following properties of atom could be explained correctly by Thomson model of atom ?

(*a*) Overall neutrality of atom.

(*b*) Spectra of hydrogen atom.

(*c*) Position of electrons, protons and neutrons in atom.

(*d*) Stability of atom.

7. Two atoms are said to be isobars if

(*a*) they have same atomic number but different mass number.

(*b*) they have same number of electrons but different number of neutrons.

(*c*) they have same number of neutrons but different number of electrons.

(*d*) sum of the number of protons and neutrons is same but the number of protons is different.

8. The number of radial nodes for 3*p* orbital is

(*a*) 3 (*b*) 4

(*c*) 2 (*d*) 1

9. Number of angular nodes for 4*d* orbital is

(*a*) 4 (*b*) 3

(*c*) 2 (*d*) 1

10. Which of the following is responsible to rule out the existence of definite paths or trajectories of electrons ?

(*a*) Pauli's exclusion principle.

(*b*) Heisenberg's uncertainty principle

(*c*) Hund's rule of maximum multiplicity.

(*d*) Aufbau principle.

11. Total number of orbitals associated with third shell will be _____

(*a*) 2 (*b*) 4

(*c*) 9 (*d*) 3

Answers

1. (*c*) **2.** (*b*) **3.** (*d*) **4.** (*d*) **5.** (*b*) **6.** (*a*) **7.** (*d*) **8.** (*d*) **9.** (*c*) **10.** (*b*) **11.** (*c*)

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12. Orbital angular momentum depends on _____ .
(a) l (b) n and l
(c) n and m (d) m and s

13. Chlorine exists in two isotopic forms, Cl-37 and Cl-35 but its atomic mass is 35.5. This indicates the ratio of Cl-37 and Cl-35 is approximately
(a) 1:2 (b) 1:1
(c) 1:3 (d) 3:1

14. The pair of ions having same electronic configuration is
(a) Cr^{3+}, Fe^{3+} (b) Fe^{3+}, Mn^{2+}
(c) Fe^{3+}, Co^{3+} (d) Sc^{3+}, Cr^{3+}

15. For the electrons of oxygen atom, which of the following statements is correct ?
(a) Z_{eff} for an electron in a 2s orbital is the same as Z_{eff} for an electron in a 2p orbital.
(b) An electron in the 2s orbital has the same energy as an electron in the 2p orbital.
(c) Z_{eff} for an electron in 1s orbital is the same as Z_{eff} for an electron in a 2s orbital.
(d) The two electrons present in the 2s orbital have spin quantum numbers m_s but of opposite sign.

16. If travelling at same speeds, which of the following matter waves have the shortest wavelength ?
(a) Electron (b) Alpha particle (He^{2+})
(c) Neutron (d) Proton

Multiple Choice Questions (Type-II)

17. Identify the pairs which are **not** of isotopes ?
(a) ${}^{12}_{6}X, {}^{13}_{6}Y$ (b) ${}^{35}_{17}X, {}^{37}_{17}Y$
(c) ${}^{14}_{6}X, {}^{14}_{7}Y$ (d) ${}^{8}_{4}X, {}^{8}_{5}Y$

18. Out of the following pairs of electrons, identify the pairs of electrons present in degenerate orbitals :
(a) (i) $n = 3, l = 2, m_l = -2, m_s = -\frac{1}{2}$
(ii) $n = 3, l = 2, m_l = -1, m_s = -\frac{1}{2}$
(b) (i) $n = 3, l = 1, m_l = 1, m_s = +\frac{1}{2}$
(ii) $n = 3, l = 2, m_l = 1\ m_s = +\frac{1}{2}$
(c) (i) $n = 4, l = 1, m_l = 1, m_s = +\frac{1}{2}$
(ii) $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$
(d) (i) $n = 3, l = 2, m_l = +2, m_s = -\frac{1}{2}$
(ii) $n = 3, l = 2, m_l = +2, m_s = +\frac{1}{2}$

19. Which of the following sets of quantum numbers are correct ?

	n	l	m_l
(a)	1	1	2
(b)	2	1	+1
(c)	3	2	−2
(d)	3	4	−2

20. In which of the following pairs, the ions are iso-electronic ?
(a) Na^+, Mg^{2+} (b) Al^{3+}, O^-
(c) Na^+, O^{2-} (d) N^{3-}, Cl^-

21. Which of the following statements concerning the quantum numbers are correct ?
(a) Angular quantum number determines the three dimensional shape of the orbital.
(b) The principal quantum number determines the orientation and energy of the orbital.
(c) Magnetic quantum number determines the size of the orbital.
(d) Spin quantum number of an electron determines the orientation of the spin of electron relative to the chosen axis.

Answers

12. (a) **13.** (c) **14.** (b) **15.** (d) **16.** (b) **17.** (c, d) **18.** (a, d) **19.** (b, c) **20.** (a, c) **21.** (a, d)

Matching Type Questions

Q.22. Match the following species with their corresponding ground state electronic configuration.

Atom / Ion	Electronic configuration
(i) Cu	(a) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}$
(ii) Cu^{2+}	(b) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2$
(iii) Zn^{2+}	(c) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$
(iv) Cr^{3+}	(d) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^9$
	(e) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^3$

Answers

(22) : (i) – (c) (ii) – (d) (iii) – (a) (iv) – (e)

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Q.23. Match the quantum numbers with the information provided by these.

Quantum number	Information provided
(*i*) Principal quantum number	(*a*) orientation of the orbital
(*ii*) Azimuthal quantum number	(*b*) energy and size of orbital
(*iii*) Magnetic quantum number	(*c*) spin of electron
(*iv*) Spin quantum number	(*d*) shape of the orbital

Q.24. Match the following rules with their statements :

Column I	Column II
(*i*) Hund's Rule	(*a*) No two electrons in an atom can have the same set of four quantum numbers.
(*ii*) Aufbau Principle	(*b*) Half-filled and completely filled orbitals have extra stability.
(*iii*) Pauli Exclusion Principle	(*c*) Pairing of electrons in the orbitals belonging to the same subshell does not take place until each orbital is singly occupied.
(*iv*) Heisenberg's Uncertainty Principle	(*d*) It is impossible to determine the exact position and exact momentum of a subatomic particle simultaneously.
	(*e*) In the ground state of atoms, orbitals are filled in the order of their increasing energies.

Q.25. Match the following :

Column I	Column II
(*i*) X-rays	(*a*) $\nu = 1 - 10^4$ Hz
(*ii*) UV	(*b*) $\nu = 10^{10}$ Hz
(*iii*) Long radio waves	(*c*) $\nu = 10^{16}$ Hz
(*iv*) Microwave	(*d*) $\nu = 10^{18}$ Hz

Q.26. Match the following :

Column I	Column II
(*i*) Photon	(*a*) Value is 4 for N shell
(*ii*) Electron	(*b*) Probability density
(*iii*) Ψ^2	(*c*) Always positive value
(*iv*) Principal quantum number n	(*d*) Exhibits both momentum and wavelength

Q.27. Match species given in Column I with the electronic configuration given in Column II.

Column I	Column II
(*i*) Cr	(*a*) $[Ar]3d^84s^0$
(*ii*) Fe^{2+}	(*b*) $[Ar]3d^{10}4s^1$
(*iii*) Ni^{2+}	(*c*) $[Ar]3d^64s^0$
(*iv*) Cu	(*d*) $[Ar]3d^54s^1$
	(*e*) $[Ar]3d^64s^2$

Answers

(23) : (*i*) – (*b*) (*ii*) – (*d*) (*iii*) – (*a*) (*iv*) – (*c*)
(24) : (*i*) – (*c*) (*ii*) – (*e*) (*iii*) – (*a*) (*iv*) – (*d*)
(25) : (*i*) – (*d*) (*ii*) – (*c*) (*iii*) – (*a*) (*iv*) – (*b*)
(26) : (*i*) – (*d*) (*ii*) – (*d*) (*iii*) – (*b*), (*c*) (*iv*) – (*a*), (*c*)
(27) : (*i*) – (*d*) (*ii*) – (*c*) (*iii*) – (*a*) (*iv*) – (*b*)

Assertion and Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below.

(*a*) Both A and R are true and R is the correct explanation of A.
(*b*) Both A and R are true but R is not the correct explanation of A.
(*c*) A is true but R is false.
(*d*) Both A and R are false.

Q.28. Assertion (A) : All isotopes of a given element show the same type of chemical behaviour.
Reason (R) : The chemical properties of an atom are controlled by the number of electrons in the atom.

Q.29. Assertion (A) : Black body is an ideal body that emits and absorbs radiations of all frequencies.
Reason (R) : The frequency of radiation emitted by a body goes from a lower frequency to higher frequency with an increase in temperature.

Q.30. Assertion (A) : It is impossible to determine the exact position and exact momentum of an electron simultaneously.
Reason (R) : The path of an electron in an atom is clearly defined.

Answers

28. (*a*) **29.** (*b*) **30.** (*c*)

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Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A1. (*b*) K.E. $= \frac{1}{2}mv^2$, P.E. $= -\frac{Ze^2}{r}$

and electrostatic force = centrifugal force

$$\frac{Ze^2}{r^2} = \frac{mv^2}{r}$$

or $$\frac{Ze^2}{r} = mv^2$$

or $$PE = -mv^2$$

$$\therefore \text{Total energy} = \frac{1}{2}mv^2 + (-mv^2) = -\frac{1}{2}mv^2$$

$$\therefore \frac{\text{K.E.}}{\text{Total energy}} = \frac{\frac{1}{2}mv^2}{-\frac{1}{2}mv^2} = -1$$

A3. (*b*) Energy emitted $= -\frac{1311.8}{3^2} - \left(-\frac{1311.8}{2^2}\right)$ kJ mol^{-1}

or $$= 1311.8\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \text{ kJ mol}^{-1}$$

$$= 1311.8\left(\frac{1}{4} - \frac{1}{9}\right)$$

$$= 1311.8 \times \frac{5}{36} \text{ kJ mol}^{-1}$$

$$\therefore \text{Energy emitted per atom} = \frac{1311.8 \times 10^3 \times 5}{6.02 \times 10^{23} \times 36} \text{J}$$

$$= 3.03 \times 10^{-19} \text{J}$$

A4. (*a*) For transition in He$^+$ (Z = 2)

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= R \times 4\left(\frac{1}{4} - \frac{1}{16}\right) = \frac{3}{4}R$$

For H atom (Z = 1)

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{3}{4}R$$

$$\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$

$\therefore n_2 = 2,\ n_1 = 1,$

A5. (*d*) I.E.$_{Li^{2+}}$ $= Z^2 \times$ I.E. (H)

$= 9 \times 13.6$ eV $= 122.4$ eV

A6. (*d*) $r_n = 0.53 \times n^2$

$\therefore r_2 = 0.53 \times 4 = 2.12$ Å

A7. (*b*) No. of spectral lines $= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

$$= \frac{(5-1)(5-1+1)}{2} = \frac{4 \times 5}{2} = 10$$

A8. (*b*) $r_n = 0.529\ n^2$Å

A9. (*c*) For H atom, first Balmer line in the series is

$$E_3 - E_2 = \frac{E_1(H)}{9} - \frac{E_1(H)}{4} = \frac{5E_1(H)}{36}$$

For He$^+$ ion (Z = 2)

$$E_6 - E_4 = \frac{-E_1(H) \times 2^2}{6^2} - \frac{E_1(H) \times 2^2}{4^2}$$

$$= -E_1(H) \times 2^2\left(\frac{16-36}{16 \times 36}\right)$$

$$= \frac{4 \times 20}{16 \times 36}E_1(H) = \frac{5E_1(H)}{36}$$

A10. (*c*) $E_n = -\frac{1.316 \times 10^6}{n^2}$

$\therefore$ Difference between first and second orbit

$$\Delta E_1 = -1.316 \times 10^6\left(\frac{1}{1} - \frac{1}{2^2}\right) = -1.316 \times 10^6 \times \frac{3}{4}$$

Difference between second and third orbit

$$\Delta E_2 = -1.316 \times 10^6\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = -1.316 \times 10^6 \times \frac{5}{36}$$

Ratio, $\frac{\Delta E_1}{\Delta E_2} = \frac{3}{4} \times \frac{36}{5} = \frac{27}{5}$

A11. (*d*) $\Delta E = h\nu = \frac{hc}{\lambda}$ or $\lambda = \frac{hc}{\Delta E}$

i.e., $\lambda \propto \frac{1}{\Delta E}$

$\Delta E = E_4 - E_1$ will be maximum and hence λ will be minimum.

A12. (*a*) Energy in the excited state is same as the K.E.

A13. (*b*) $r_n = 0.059\ n^2$

$r_1 = 0.059,\ r_2 = 0.059 \times 4,\ r_3 = 0.059 \times 9$

$\therefore \quad r_1 : r_2 : r_3 = 1 : 4 : 9$

A14. (*d*) Frequency of a line in spectral series can be calculated as

$$\nu = \frac{c}{\lambda} = cR_H(Z)^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For third line in Lyman series,

$$n_1 = 1, n_2 = 4$$

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$$\nu_H = c.R_H(1)^2\left[\frac{1}{1^2}-\frac{1}{4^2}\right]=\frac{15}{16}R_HC$$

For first line in Balmer series for Li^{2+}

$$n_1 = 2, n_2 = 3$$

$$\nu_{Li^{2+}} = cR_H(Z)^2\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

$$= cR_H(3)^2\left[\frac{1}{2^2}-\frac{1}{3^2}\right]$$

$$= c\times R_H\times 9\times\frac{5}{36}=\frac{5}{4}cR_H$$

$$\frac{\nu_H}{\nu_{Li^{2+}}}=\frac{15}{16}\times\frac{4}{5}=\frac{3}{4}$$

A15. (*c*) Energies are additive so that

$$E_3 = E_1 + E_2$$

$$\frac{hc}{\lambda_3}=\frac{hc}{\lambda_1}+\frac{hc}{\lambda_2}$$

or $$\frac{1}{\lambda_3}=\frac{1}{\lambda_1}+\frac{1}{\lambda_2}=\frac{\lambda_1+\lambda_2}{\lambda_1\lambda_2}$$

$$\lambda_3=\frac{\lambda_1\lambda_2}{\lambda_1+\lambda_2}$$

A16. (*d*) $\lambda = \frac{h}{mv}$ or $v = \frac{h}{\lambda m}$

$$\therefore v=\frac{6.6\times10^{-34}}{9.0\times10^{-31}\times600\times10^{-9}}=1.22\times10^3\ ms^{-1}$$

A18. (*d*) $\Delta x\times\Delta p=\frac{h}{4\pi}$

or $\Delta p=\frac{h}{4\pi\Delta x}=\frac{h}{4\pi\times0}=\infty$

A24. (*b*) No. of orbitals in a shell = $2l + 1$

No. of electrons in a shell = $2(2l + 1) = 4l + 2$

A25. (*a*) It corresponds to 6*d*-orbitals and, therefore, can accommodate maximum of 10 electrons.

A26. (*c*) 4*d* has highest energy.

A28. (*d*) $n = 7, l = 2$ corresponds to 7*d* and not 7*p*

A29. (*a*) Because $l = 0$ for *s* electrons.

Orbital angular momentum = $\sqrt{l(l+1)}.\frac{h}{2\pi}=0$

A30. (*a*) One set of quantum numbers represents only one orbital.

A32.(*a*) Electronic configuration of Mn (Z = 25) is $1s^22s^22p^63s^23p^63d^54s^2$

Total orbitals populated

$= 1 + 1 + 3 + 1 + 3 + 5 + 1 = 15$

A33. (*d*) Fe^{3+} has $3d^5$ configuration and, therefore, has 5 (maximum) number of electrons while Mg^{2+} has zero, Ti^{3+} has $1(3d^1)$ and V^{3+} has $2(3d^2)$.

A34. (*b*) The last electron in Na atom is present in 3*s* subshell *i.e.*, $l = 0$

A36. (*b*) The electronic configuration of Ar is : $1s^22s^22p^63s^23p^6$

No. of electrons having $m = 0$ are

$= 2(1s) + 2(2s) + 2(2p_z) + 2(3s) + 2(3p_z) = 10$

A38. (*a*) No. of unpaired electrons :

1. Ni^{2+} (Z = 28) : [Ar] $3d^8 = 2$
2. Co^{2+} (Z = 27) : [Ar] $3d^7 = 3$
3. Cr^{2+} (Z = 24) : [Ar] $3d^4 = 4$
4. Fe^{3+} (Z = 26) : [Ar] $3d^5 = 5$

$\therefore$ Correct order = 1, 2, 3, 4

A39. (*d*) It corresponds to 3*p* (3), 3*d* (5), 4*s* (1), 4*p* (3), 5s (1) = 13

A41. (*d*) No. of nodes = $n - l - 1 = 3 - 2 - 1 = 0$

A43. (*c*) Radial nodes = $n - l - 1 = 3 - 1 - 1 = 1$

Angular nodes = $l = 1$

A44. (*b*) Electronic configuration of Cr (Z = 24):

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4d^5\ 4s^1$

No. of electrons with $l = 1$ are $6(2p^6) + 6(3p^6) = 12$

No. of electrons with $l = 2$ are 5 $(3d^5)$

A46. (*c*) No. of nodes = $n - l - 1 = 4 - 0 - 1 = 3$

B. *mcq from competitive examinations*

B1. (*a*) $\lambda=\frac{h}{\sqrt{2K.E.m}}=\frac{6.626\times10^{-34}}{\sqrt{2\times0.5\times1}}=6.626\times10^{-34}\ m$

B2. (*b*) (B) Value of l cannot be equal to n

(D) For $l = 0$, m cannot be -1

(E) For $l = 2$, m cannot be 3

B3. (*e*) $\frac{1}{2}mv^2 = h(\nu-\nu_0)$

$6.63\times10^{-20}\ kg\ m^2s^{-2}$

$= 6.63\times10^{-34}\ kg\ m^2\ s^{-1}(2\times10^{14}-\nu_0)$

$$\frac{6.63\times10^{-20}}{6.63\times10^{-34}}=2\times10^{14}-\nu_0$$

$1\times10^{14}-2\times10^{14}=-\nu_0$ or or $\nu_0 = 1\times10^{14}\ s^{-1}$

B4. (*a*)

$$\Delta x = \Delta p$$

$$\Delta x\,.\,\Delta p = \frac{h}{4\pi}$$

$$\Delta p\,.\,\Delta p = \frac{h}{4\pi}$$

$$\Delta p^2 = \frac{h}{4\pi}$$

$$\Delta p = \sqrt{\frac{h}{4\pi}}$$

$$m\Delta v = \sqrt{\frac{h}{4\pi}}$$

$$\Delta v = \frac{1}{2m}\sqrt{\frac{h}{\pi}}$$

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B5. (*a*) $\Delta p = m\Delta v = 1 \times 10^{-18}$ g cm s^{-1}

$$\Delta v = \frac{1\times10^{-18}\text{ g cm s}^{-1}}{9\times10^{-28}\text{ g}}$$

$$\therefore \quad = 1\times10^{9}\text{ cm s}^{-1}$$

B6. (*e*) $\lambda = \dfrac{h}{mv}$

$m_A = x \quad v_A = 0.1 \quad m_A v_A = 0.1\,x$

$m_B = 5x \quad v_B = 0.05 \quad m_B v_B = 0.25\,x$

$$\frac{\lambda_A}{\lambda_B} = \frac{m_B v_B}{m_A v_A} = \frac{0.25x}{0.1x} = \frac{25}{10} = \frac{5}{2}$$

B7. (*d*) Maximum number of electrons in a subshell $= 2(2l + 1)$ or $4l + 2$

B8. (*b*) For $l = 2$, $m = -3$ is not possible.

B9. (*b*) Co : [Ar]$3d^7 4s^2$

Co^{3+} : [Ar] $3d^6$

B10. (*b*) No. of orbitals in an energy level = n^2.

$\therefore$ No. of orbitals in 4th energy level = $4^2 = 16$

B11. (*b*) $E_1 = \dfrac{hc}{\lambda_1}$, $E_2 = \dfrac{hc}{\lambda_2}$

$$\frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1} \quad \text{or} \quad \frac{\lambda_2}{\lambda_1} = \frac{25}{50} = \frac{1}{2}$$

$\therefore \quad \lambda_1 = 2\lambda_2$

B12. (*a*) For $n = 6$

$6s \longrightarrow 4f \longrightarrow 5d \longrightarrow 6p$

B13. (*a*) This corresponds to $4f$ subshell and therefore, it can have 14 electrons.

B14. (*c*) The electronic configuration of Rb is [Ar]$3d^{10}4s^2 4p^6 5s^1$. The outermost electron is $5s^1$.

Quantum numbers : 5, 0, 0, $+\dfrac{1}{2}$.

B15. (*b*) The orbital associated with $n = 3$, $l = 1$ is $3p$. The number of electrons with $m = -1$ is 2.

B16. (*b*) The electron is more tightly bound in the smallest allowed orbit.

B17. (*a*) $\nu = \dfrac{c}{\lambda}$ or $\lambda = \dfrac{c}{\nu}$

$$\lambda = \frac{3\times10^{17}\text{ nm s}^{-1}}{6\times10^{15}\text{ s}^{-1}} = 50\text{ nm}.$$

B18. (*d*) Deuterium has 1 proton and 1 neutron α-particle has 2 protons and 2 neutrons

$\therefore$ Mass of α-particle (m_α) is twice that of deuterium (m_D) *i.e.* $m_\alpha = 2m_D$

Also, velocity of deuterium (v_D)

= 5 times velocity of α-particle (v_α)

i.e. $v_D = 5v_\alpha$ or $v_\alpha = v_D/5$

$$\lambda_D = \frac{h}{m_D v_D} \text{ and}$$

$$\lambda_\alpha = \frac{h}{m_\alpha v_\alpha} = \frac{h}{(2m_D)\left(\frac{v_D}{5}\right)}$$

or $$\frac{\lambda_D}{\lambda_\alpha} = \frac{h}{m_D v_D}\times\frac{(2m_D)(v_D)}{5h} = 0.4$$

B19. (*d*) $m = 6.626 \times 10^{-31}$ kg

$\Delta v = 1 \times 10^6$ ms^{-1}

$\Delta x = ?$

$$\Delta x.\, m\Delta v = \frac{h}{4\pi}$$

$$\text{or } \Delta x = \frac{h}{4\pi m\Delta v} = \frac{6.626\times10^{-34}}{4\times\pi\times6.626\times10^{-31}\times10^{6}} = \frac{1\times10^{-9}\text{ m}}{4\pi} = \left(\frac{1}{4\pi}\right)\text{nm}$$

B20. (*a*) It represents $3p_z$ orbital.

B21. (*d*) $E = \dfrac{hc}{\lambda} = \dfrac{6.626\times10^{-34}\times3\times10^{8}}{45\times10^{-9}} = 4.42\times10^{-18}$ J

B22. (*b*) $\mu = \sqrt{n(n+2)} = 2.83$

or $n(n+2) = (2.83)^2 = 8$

or $n = 2$

Ni^{2+} has [Ar] $3d^8$ configuration. Therefore, it has two unpaired electrons.

B23. (*c*) $n = 3, l = 0, m_l = 0, m_s = +\dfrac{1}{2}$ is possible and all other are not possible.

B24. (*c*) Orbital angular momentum = $\sqrt{l(l+1)}\,\hbar$

For a *d*–orbital, $l = 2$

$\therefore$ Orbital angular momentum = $\sqrt{2(2+1)}\hbar$

$= \sqrt{6}\,\hbar$

B25. (*a*) After filling electrons in titanium, the configuration is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^1\,4s^2$

So, correct order of orbitals in titanium is $3s$, $3p$, $3d$ $4s$

B26. (*d*) Fe^{2+} : [Ar]$3d^6$

Number of *d*–electrons = 6

Fe : [Ar] $3d^6\,4s^2$ (No. of *d*-electrons = 6)

Ne : $1s^2\,2s^2\,2p^6$ (No. of *p*-electrons = 6)

Mg : $1s^2\,2s^2\,2p^6\,3s^2$ (No. of *s*-electrons = 6)

Cl : $1s^2\,2s^2\,2p^6\,3s^2\,3p^5$ (No. of *p*-electrons = 11)

B28. (*a*) For $n = 3$ and $l = 1$, the subshell is $3p$ and a particular $3p$ orbital can accommodate only 2 electrons.

B29. (*c*) $d_{x^2-y^2}$ and d_{z^2} orbitals have electron density along the axes. d_{xy}, d_{yz} and d_{zx} orbitals have electron density between the axes.

B30. (*c*) The energy of 2s-orbital and 2*p*-orbital is equal in hydrogen like atoms.

B31. (*c*) Option (*c*) is wrong according to Hund's rule.

B33. (*c*) Angular momentum in nth orbit = $\dfrac{nh}{2\pi}$

$\therefore$ Angular momentum in 5th orbit = $\dfrac{5h}{2\pi}$ = **2.5 h/π**

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B34. (*b*) $\Delta x = \dfrac{h}{4\pi m \Delta v}$

$\Delta v = \dfrac{300 \times 0.001}{100} = 3 \times 10^{-3}\ \text{ms}^{-1}$

$\Delta x = \dfrac{6.63 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 3 \times 10^{-3}}$

$= \mathbf{1.93 \times 10^{-2}\ m}$

B35. (*e*) For H- like species, $r_n = \dfrac{0.529\ n^2}{Z}$ Å

r_3 for He^+ (Z = 2) $= \dfrac{0.529 \times 3^2}{2}$

$= \mathbf{2.38\ Å}$

B37. (*a*) $\Delta E = E_2 - E_1 = -\dfrac{1.312 \times 10^6}{2^2} - \left(-\dfrac{1.312 \times 10^6}{1^2}\right)$

$= 9.85 \times 10^5\ \text{J mol}^{-1}$.

B38. (*c*) $\Delta v = \dfrac{0.005}{100} \times 600 = 0.03$

$\Delta x \times m\Delta v = \dfrac{h}{4\pi}$

$\Delta x = \dfrac{h}{4\pi m \Delta v}$

$= \dfrac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 0.03}$

$= 1.92 \times 10^{-3}\ \text{m}$

B39. (*b*) $\lambda = \dfrac{h}{mv} = \dfrac{6.63 \times 10^{-34}}{1.67 \times 10^{-27} \times 1 \times 10^3}$

$= 3.9 \times 10^{-10}\ \text{m}$

$\approx 4 \times 10^{-10}\ \text{m} = 0.40\ \text{nm}$

B40. (*a*) Number of spectral lines emitted when electron jumps from n_2 to n_1

$= \dfrac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

$= \dfrac{(5-1)(5-1+1)}{2} = 10$ lines

B41. (*a*) $\bar{\nu} = R_H\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right] = \dfrac{8}{9}R_H$

$\therefore \quad \dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} = \dfrac{8}{9}$

$\therefore \quad n_1 = 1$

$n_2 = 3$

B42. (*d*) $\bar{\nu} = 109678\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

Wavelength is shortest when $n_1 = 1$ and $n_2 = \infty$

$\therefore \quad \bar{\nu} = 109678\left(\dfrac{1}{1^2} - \dfrac{1}{\infty^2}\right)$

$= 109678\ \text{cm}^{-1}$

$\lambda = \dfrac{1}{\bar{\nu}}$

$= \dfrac{1}{109678}\text{cm} = 911.7 \times 10^{-8}\ \text{cm}$

$= 911.7\ \text{Å}$.

B43. (*d*) IE of He^+ ion = IE of H atom $\times Z^2$

= I.E of H atom $\times (2)^2$

$19.6 \times 10^{-18}\ \text{J atom}^{-1} = 4 \times$ I.E. of H atom

$\therefore$ I.E of H atom $= \dfrac{19.6 \times 10^{-18}}{4}$

$= 4.9 \times 10^{-18}\ \text{J atom}^{-1}$

I.E of Li^{2+} ion = I.E of H atom $\times (3)^2$

I.E of Li^{2+} ion $= 4.9 \times 10^{-18} \times 9$

$= 4.41 \times 10^{-17}$ J

Energy = -4.41×10^{-17} J

B44. (*e*) For He^+, $\dfrac{1}{\lambda} = Z^2R\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

$\dfrac{1}{\lambda} = 2^2R\left(\dfrac{1}{2^2} - \dfrac{1}{4^2}\right) = \dfrac{3R}{4}$

For H atom, $\dfrac{1}{\lambda} = R\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right) = \dfrac{3R}{4}$

or $\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} = \dfrac{3}{4}$

$\therefore\ n_1 = 1,\ n_2 = 2$

B45. (*c*) 1. Beyond a certain wavelength, line spectrum appears as band spectrum.

2. For Balmer series $n_1 = 2$.

4. For line of longest wavelength (lowest energy) in this series, $n_2 = 3$.

B46. (*a*) ν (H) = ν (He^+)

$RZ^2\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)_H = RZ^2\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)_{He^+}$

$\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} = 4\left(\dfrac{1}{4} - \dfrac{1}{16}\right)$

$\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} = 1 - \dfrac{1}{4} = \dfrac{3}{4}$

$\therefore\ n_1 = 1$ and $n_2 = 2$

B47. (*d*) For third line in Lyman series,

$n_1 = 1, n_2 = 4$

$\nu_H = \dfrac{c}{\lambda} = c.R_HZ^2\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

$= c.R_H(1)^2\left[\dfrac{1}{1^2} - \dfrac{1}{4^2}\right] = \dfrac{15}{16}\ R_Hc$

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For first line in Balmer series for Li^{2+}

$n_1 = 2, n_2 = 3$

$$\nu_{Li^{2+}} = cR_H(Z)^2\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

$$= cR_H(3)^2\left[\frac{1}{2^2}-\frac{1}{3^2}\right] = c\times R_H\times 9\times\frac{5}{36} = \frac{5}{4}cR_H$$

$$\frac{\nu_H}{\nu_{Li^{2+}}} = \frac{15}{16}\times\frac{4}{5} = \frac{3}{4}$$

B48. (*d*) The electronic configuration of Na is: $1s^2\,2s^2\,2p^6\,3s^1$
The outermost electron is $3s^1$.

Quantum numbers : 3, 0, 0, $\frac{1}{2}$

B49. (*a*) The orbitals are (1) 4*p* (2) 4*s* (3) 3*d* (4) 3*p*.
Increasing order of energies is :
(4) 3*p* < (2) 4*s* < (3) 3*d* < (1) 4*p*.

B50. (*b*) Cu : [Ar] $3d^{10}\,4s^1$
Cu^{2+} : [Ar] $3d^9\,4s^0$

B51. (*b*) $E_n = -\frac{2\pi^2me^4}{n^2h^2}(Z^2)$

or $E_n \propto -\frac{Z^2}{n^2} = -\frac{kZ^2}{n^2}$

I.E. of $He^+ = E_\infty - E_1$

$$= 0 - \left(-\frac{k(2)^2}{1^2}\right) = 4k$$

$4k = 19.60\times10^{-18}$ J atom^{-1}

or $k = \frac{19.60\times10^{-18}}{4} = 4.9\times10^{-18}$ J atom^{-1}

For Li^{2+}, Z = 3 and first energy state, $n = 1$

$$\therefore\quad E_1 = -k\frac{Z^2}{n^2} = -\frac{4.9\times10^{-18}\times3^2}{1^2}$$

$= -44.1\times10^{-18}$ J atom^{-1}

I.E. of $Li^{2+} = E_\infty - E_1 = 0 - (-44.1\times10^{-18})$
$= 44.1\times10^{-18}$ J atom^{-1}.

B52. (*c*) According to Aufbau principle, in the ground state of the atom, the orbitals are filled in order of their increasing energies. Therefore, electron should completely fill *ns* orbitals before going to *np* orbitals.

B53. (*b*) $E_1 = -2.178\times10^{-18}\times\frac{1^2}{1^2} = -2.178\times10^{-18}$ J

$E_2 = -2.178\times10^{-18}\times\frac{1^2}{2^2} = -5.445\times10^{-19}$ J

Energy required to excite electron from $n = 1$ to $n = 2$,

$\Delta E = -5.445\times10^{-19} - (-2.178\times10^{-18})$
$= 16.335\times10^{-19}$ J

$\frac{hc}{\lambda} = 16.335\times10^{-19}$

$$\lambda = \frac{6.63\times10^{-34}\times3.0\times10^8}{16.335\times10^{-19}}$$

$= 1.217\times10^{-7}$ m

B54. (*c*) $\lambda = \frac{h}{mv}$

$m = 100$ g $= 0.1$ kg $\qquad v = 100$ cm $s^{-1} = 1$ ms^{-1}

$$\lambda = \frac{6.6\times10^{-34}}{0.1\times1} = 6.6\times10^{-33}\text{ m} = 6.6\times10^{-31}\text{ cm}$$

B55. (*d*) $\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$

Shortest wavelength line in hydrogen spectrum of Lyman series is from $n_2 = \infty$ and $n_1 = 1$

$$\frac{1}{\lambda} = 109678\left[\frac{1}{(1)^2}-\frac{1}{\infty^2}\right] = 109678\text{ cm}^{-1}$$

or $\lambda = \frac{1}{109678}$ cm $= 9.11\times10^{-6}$ cm

$= 911\times10^{-10}$ m or 911 Å

B56. (*b*) The electronic configuration of Rb (Z = 37) is
$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,5s^1$
Valence electron is $5s^1$
Quantum numbers ;
$n = 5,\ l = 0,\ m = 0,\ s = +½$

B57. (*a*) For first excited state of hydrogen ($n = 2$)

$$\text{Energy} = \frac{-13.6}{n^2}\text{ eV} = \frac{-13.6}{(2)^2} = -3.4\text{ eV}$$

B58. (*c*) Time taken to complete one revolution

$$t = \frac{\text{Circumference}}{\text{Velocity}}$$

$$t = \frac{2\pi r}{v}$$

Now $mvr = \frac{nh}{2\pi}$

or $v = \frac{nh}{2\pi mr}$

$$\therefore\quad t = \frac{2\pi r\times2\pi mr}{nh} = \frac{4\pi^2mr^2}{nh}$$

B61. (*d*) For $l = 2$, m cannot have a value of –3. The only permissible values of m for $l = 2$ are:
–2, –1, 0, +1, +2

B62. (*d*) An electron of charge '*e*' is passed through a potential difference of V, then its kinetic energy becomes eV.

$$\frac{1}{2}mv^2 = eV$$

or $v = \sqrt{\frac{2eV}{m}}$

According to de-Broglie,

$$\lambda = \frac{h}{mv} = \frac{h}{m\sqrt{\frac{2eV}{m}}}$$

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or $\lambda = \dfrac{h}{\sqrt{2meV}}$

$\therefore \quad \dfrac{h}{\lambda} = \sqrt{2meV}$

B63. (*a*) (*i*) 4*p* orbital (*ii*) 4*s* orbital (*iii*) 3*d*-orbital (*iv*) 3*p*-orbital
Order of increasing energy
3*p* (*iv*) < 4*s* (*ii*) < 3*d* (*iii*) < 4p (*i*)

B64. (*b*) Electronic configuration of Cr (Z = 24)
Cr : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$
19th electron is present in 4*s*-orbital
For 4*s* orbital; $n = 4, l = 0, m = 0, s = \pm ½$

B65. (*d*) Cl (Z = 17) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
The unpaired electron of Cl is in 3*p* orbtial.
Hence, quantum numbers for unpaired electron are:

$n = 3, l = 1, m = +1, 0, -1, s = +\dfrac{1}{2}$ or $-\dfrac{1}{2}$

B66. (a) $E_n = -\dfrac{13.6}{n^2}$ eV

For 3*s*-orbital, $n = 3$

$$E_n = -\frac{13.6}{3^2} = -1.51\text{eV}$$

B67. (*d*) $r = \dfrac{0.529n^2}{Z}$

$Z = 1, \quad n = 2$

$$r = \frac{0.529 \times (2)^2}{1} = 2.12\text{Å}$$

B68. (*c*) For $n = 2, l = 0$, *m* cannot be –1 because m has values $-l \ldots .0 \ldots\ldots + l$

B69. (*b*) Ni (28) : [Ar] $4s^2\ 3d^8$
No. of unpaired electrons = 2.

B70. (*c*) For Lyman series electrons return from $n = 2, 3, 4, 5$ to $n = 1$.

B72. (*b*)

$$h\nu = w_0 + \frac{1}{2}mv^2$$

$$w_o = h\nu - \frac{1}{2}mv^2$$

$$= \frac{6.626 \times 10^{-34} \times 3.0 \times 10^8}{4000 \times 10^{-10}} - \frac{1}{2} \times 9 \times 10^{-31} \times (6 \times 10^5)^2$$

$$= 4.96 \times 10^{-19} - 1.62 \times 10^{-19} = 3.34 \times 10^{-19}\text{J}$$

or $\dfrac{3.34 \times 10^{-19}}{1.6 \times 10^{-19}} = 2.1$ eV

B73. (*d*) Radius of an orbit,

$$r = \frac{0.529n^2}{Z}\ \text{Å}$$

For H atom Z = 1

$$r_1 = 0.529\, n^2\ \text{Å}$$

For Be^{3+}, Z = 4

$$r_{Be^{3+}} = \frac{0.529n^2}{4}\ \text{Å}$$

Given that $r_H = r_{Be^{3+}}$
$\therefore$ It is equal when $n = 2$ for Be^{3+}
$\therefore\ r_2(Be^{3+}) = r_1(H)$

B75. (*c*) For Bohr orbit, angular momentum is

$$mvr_n = \frac{nh}{2\pi} \quad \text{or} \quad v = \frac{nh}{2\pi mr_n}$$

Kinetic energy, $KE = \dfrac{1}{2}mv^2$

or $\text{K.E.} = \dfrac{1}{2}m \times \dfrac{n^2h^2}{4\pi^2m^2r_n^2} = \dfrac{n^2h^2}{8\pi^2mr_n^2}$

For $n = 2, r_n = a_0 \times n^2 = 4a_0$ (a_0 = Bohr radius)

$$\text{K.E.} = \frac{2^2h^2}{8\pi^2m(4a_0)^2} = \frac{h^2}{32\pi^2ma_0^2}$$

C. *mcq with more than one correct answer*

C3. (*b, c*) : (*b*) 3*p* and 4*d* have 1 node (c) 4*s* and 5*p* have 3 nodes.

C4. (*b, c*) : No. of unpaired electrons : $Cr^{3+}(3)$, $Fe^{2+}(4)$, $Cu^{+}(0)$, $Zn^{2+}(0)$, $Mn^{2+}(5)$, $Fe^{3+}(5)$, $Sc^{3+}(0)$, $Ti^{3+}(1)$.

C5. (*a, c*) : O^{2-} and Na^+ have 10 electrons.

C6. (*a, b*) : No. of unpaired electrons : Cu (1), Sc (1), Mn (5), Cr (6).

C7. (*a, d*) : (*a*) $4d > 5s$ (*b*) $3d = 3p$ (*c*) $3p = 3d$ (*d*) $3d > 2p$.

C8. (*a, b, c*) : (*d*) is not correct. The spacing between adjacent levels decreases with increase in '*n*'.

D. *mcq based on comprehension*

D1. (*b*) Wavelength of α-particles

$$\lambda\ (\alpha\text{-particle}) = \frac{h}{mv} = \frac{h}{6.6 \times 10^{-27} \times 2.5 \times 10^2}$$

$$\lambda\ (\text{photon}) = \frac{h}{m \times 3.0 \times 10^8}$$

Since $\lambda(\alpha\text{-particle}) = \lambda\ (\text{photon})$

$$\frac{h}{6.6 \times 10^{-27} \times 2.5 \times 10^2} = \frac{h}{m \times 3.0 \times 10^8}$$

$$m = \frac{6.6 \times 10^{-27} \times 2.5 \times 10^2}{3.0 \times 10^8}$$

$$= \mathbf{5.5 \times 10^{-33}\ kg}$$

D2. (*b*) Wavelength of electron accelerated by potential of V volt is

$$\lambda = \frac{h}{(2\ \text{Vem})^{1/2}} = \frac{h}{(2 \times 100 \times 10^6 em)^{1/2}} = \frac{h \times 10^{-4}}{(2\ me)^{1/2}}$$

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D3. (*d*) $\lambda_p = \frac{h}{(2\pi\, Ve\, m_p)^{1/2}}$,

$$\lambda_{He^{2+}} = \frac{h}{(2\pi\, Ve\, m_{He^{2+}})^{1/2}} = \frac{h}{(2\pi Ve\, 4m_p)^{1/2}}$$

$$\therefore \frac{\lambda He^{2+}}{\lambda_p} = \frac{(2\pi\, Ve\, m_p)^{\frac{1}{2}}}{(2\pi\, Ve\, 4m_p)^{\frac{1}{2}}} = \mathbf{\frac{1}{2}}$$

D4. (*c*) $mvr = n\frac{h}{2\pi} = \frac{4h}{2\pi}$

$$\therefore \quad r = \frac{2h}{\pi mv} = \frac{2}{\pi\lambda}$$

D5. (*a*) $m = \frac{4}{6.022\times10^{23}} = 6.64\times10^{-27}$ kg

$$\lambda = \frac{6.6\times10^{-34}}{6.64\times10^{-27}\times2.0\times10^{4}} = 4.99\times10^{-12}\text{m}$$

$$= \mathbf{4.99\ pm}$$

D6. (*c*) For 3*s* electron, $l = 0$ so that orbital angular momentum $\sqrt{l(l+1)}\ \frac{h}{2\pi}$ is zero.

D7. (*b*) $n + l = 5$ is possible for 5*s*, 4*p* and 3*d*.

D8. (*c*) For 4*f* electron, $n = 4$, $l = 3$, $m_l = 0$ and $s = +\frac{1}{2}$ is possible.

D9. (*b*) S_1 state is 2*s* because in 2*s* orbital, there is one node $(n - l - 1) = 2 - 0 - 1 = 1$

D10. (*c*) Energy in S_1 state

$$E = -\frac{13.6\times3^2}{2^2}$$

$$= -\frac{9}{4}\times13.6\,eV$$

$$E_H = -13.6\text{ eV (ground state)}$$

$$E = -\frac{9}{4}\times E_H = 2.25\ E_H$$

D11. (*b*) S_2 state is 3*p* state

Orbital angular momentum quantum number = 1

D12. (*d*) The 1*s*-orbital is non-directional and its wave function is independent of cos θ. Hence (*d*) is incorrect.

D13. (*d*) For hydrogen like species, only (*d*) is correct.

In (*a*) 1*s* orbital has no radial node.

In (*b*) for $3d_{z^2}$, *xy* is not a nodal plane.

In (*c*) $2p_z$ has no radial node.

D14. (*d*) Energy needed when electron is excited from $n = 2$ to $n = 4$ state.

$$E_4 - E_2 = R\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = \frac{3}{16}R$$

Energy needed when electron is excited from $n = 2$ to $n = 6$ state.

$$E_6 - E_2 = R\left(\frac{1}{2^2} - \frac{1}{6^2}\right) = \frac{8}{36}R$$

$$\frac{E_4 - E_2}{E_6 - E_2} = \frac{3}{16}\times\frac{36}{8} = \frac{27}{32}$$

Hence $E_4 - E_2 = \frac{27}{32}\times(E_6 - E_2)$

Integer Type Questions

- **1** (9) : No. of orbitals in a shell in $n = 3$ will be $= n^2$ *i.e.*, $3^2 = 9$. Each orbital can have maximum of two electrons, one with $m_s = +\frac{1}{2}$ and the second with $m_s = -\frac{1}{2}$. Hence number of electrons with $m_s = +\frac{1}{2}$ will be 9.
- **2** (4) : Ionization energy of He^+ ion $= Z^2 \times$ I.E. (H) $= 2^2 \times$ I.E. (H) = 4 times
- **3** (7) : For *f*-subshell, $l = 3$ and hence it has $(2\times3 + 1) = 7$ times
- **4** (4) : Fe^{2+} : [Ar] $3d^6$. Hence, it has four unpaired electrons.
- **5** (6) : It corresponds to *p*-subshell and hence has maximum of 6 electrons.
- **6** (6) : Angular momentum is $\sqrt{l(l+1)}\ \frac{h}{2\pi}$

  Since $l = 2$ for 3*d* orbital

  Angular momentum $= \sqrt{2(2+1)}\ \frac{h}{2\pi} = \sqrt{6}\ \frac{h}{2\pi}$.
- **7** (9) : $r_n = a_0\frac{n^2}{Z}$

  For H, Z = 1 and for $n = 3$

  $r_3 = a_0 \times 3^2 = 9a_0$.
- **8** (5) : $\lambda = \frac{h}{mv}$

  $\frac{1}{2}mv^2 = KE$

  $mv^2 = 2KE$

  $m^2v^2 = 2m\ KE$

  $\therefore \quad mv = \sqrt{2\ m\ KE}$

  $\therefore \quad \lambda = \frac{h}{\sqrt{2m.KE}}$

  Now K.E. $\propto$ T

  $\lambda \propto \frac{h}{\sqrt{2mT}}$

  $\lambda_{He} \propto \frac{h}{\sqrt{2m_{He}T_{He}}}$

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Competition File

$$\lambda_{Ne} \propto \frac{h}{\sqrt{2m_{Ne}T_{Ne}}}$$

$$\frac{\lambda_{He}}{\lambda_{Ne}} \propto \sqrt{\frac{m_{Ne}T_{Ne}}{m_{He}T_{He}}}$$

$$T_H = 273 - 73 = 200\ K,$$

$$T_{Ne} = 727 + 273 = 1000$$

$$\frac{\lambda_{He}}{\lambda_{Ne}} = \sqrt{\frac{20\times1000}{4\times200}}$$

$$\frac{\lambda_{He}}{\lambda_{Ne}} = 5$$

$$\therefore \quad \lambda_{He} = 5\,\lambda_{Ne}$$

- **9** (3) : For $n = 4$; $l = 0, 1, 2, 3$.
Except $l = 0$, all other 'l' values can have $m_l = 1$. Therefore, three orbitals of $n = 4$ can have $m_l = 1$. Each of these orbitals can accommodate one electron with $m_s = -\frac{1}{2}$. Thus, the total number of electrons is three.

- **10** (3) : In 'H' atom, there is only 1 electron ($1s^1$). Therefore, there is no screening effect. Due to this, energy of all subshells in a given shell is same. Thus, order of energy of various sub-shells is

$$1s < 2s = 2p < \underbrace{3s = 3p = 3d}_{\text{Same energy}} < 4s = 4p = 4d = 4f$$

The second excited state of hydrogen corresponds to the third energy level. It has 9 orbitals of same energy (one $3s$, three $3p$, five $3d$: Total = 1 + 3 + 5 = 9 orbitals). Thus, degeneracy is 9.
In H^-, there are two electrons. Thus, screening effect is present. Therefore, order of energy of various sub-shells is
$1s < 2s < 2p < 3s < 3p$ ------
First excited state for H would be : $1s^1\ 2s^1$
Second excited state for H^- would be $1s^1, 2s^0, 2p^1$
Degeneracy of a p-subshell is 3.

NCERT Exempler Problems : MCQs Type-I

1. (c) The concept of circular paths of fixed energy was proposed by Bohr and not derived from Rutherford's scattering experiment.

2. (b) Correct configuration in ground state should be $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$.

3. (d) The probability density of electrons in $2s$ orbit first increases, then decreases and after that it begins to increase again.

6. (a) Thomson model of atom could explain only the overall neutrality of the atom.

8. (d) No. of radial nodes in $3p = n - l - 1$
or $3 - 1 - 1 = 1$

11. (c) No. of orbitals in 3rd shell ($n = 3$) = $n^2 = 3^2 = 9$.

13. (c) If Cl-37 and Cl-35 exist in the ratio of 1:3, then average atomic mass comes out to be 35.5.

14. (b) Cr^{3+} : [Ar]$3d^3$, Fe^{3+} : [Ar]$3d^5$; Mn^{2+} : [Ar]$3d^5$
Thus, Mn^{2+} and Fe^{3+} have same electronic configuration.

16. (b) $\lambda \propto \frac{1}{m}$ so that alpha particles having larger mass has shortest wavelength.

NCERT Exempler Problems : MCQs Type-II

17. (c, d) are not isotopes because they have different atomic numbers.

18. (a, d) : Degenerate orbitals have same n and same l values.

20. (a, c)
$Na^+ = 11 - 1 = 10\ e^-$, $Mg^{2+} = 12 - 2 = 10e^-$, *i.e.* have same no. of electrons.
$Al^{3+} = 13 - 3 = 10\ e^-$, $O^{2-} = 8 + 1 = 9\ e^-$ *i.e.* do not have same no. of electrons.
$Na^+ = 11 - 1 = 10\ e^-$, $O^{2-} = 8 + 2 = 10\ e^-$ *i.e.* have same no. of electrons.
$N^{3-} = 7 + 3 = 10\ e^-$, $Cl^- = 17 + 1 = 18\ e^-$ *i.e.* do not have same no. of electrons.

NCERT Exemplar Problems: Matching Type

25. Frequency decreases in the order : X-rays > UV-rays > microwaves > radiowaves.

26. Photon has particle as well as wave nature. Electron has also particle as well as wave nature. ψ^2 represents probability density and is always positive. Principle quantum number n = 4 for N shell and always has positive values.

27. Cr : [Ar] $3d^5$, Fe^{2+} : [Ar] $3d^6 4s^0$; Ni^{2+} = [Ar] $3d^8 4s^0$; Cu = [Ar] $3d^{10} 4s^1$.

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Unit Practice Test

for Board Examination

Time Allowed: 1 Hr. ***Maximum Marks: 25***

1. What do you mean by the statement that energy of the electron is quantized? (1)

2. What is energy of a photon of light having frequency $3.0 \times 10^{15}\ s^{-1}$ (Planck's constant = 6.6×10^{-34} Js)? (1)

3. How many neutrons and protons are present in $^{235}_{92}U$? (1)

4. Which has larger wavelength : an electron or a proton? (1)

5. What is the designation of an orbital having $n = 4$ and $l = 2$? (1)

6. What are the permitted values of n, l and m_l for an electron in a 4*f* orbital? (2)

7. Calculate the wavelength associated with an electron (mass = 9.1×10^{-31} kg) having kinetic energy 3.0×10^{-25} J. (2)

8. Write the electronic configurations and predict the number of unpaired electrons in the following:
(*ii*) Cr (Z = 24)
(*ii*) Fe (Z = 26) (2)

9. What is an orbital? Compare the shapes of 1*s* and 2*s*-orbital. (3)

10. An electron has a speed of 600 ms^{-1} with uncertainty of 0.025%. What is the uncertainty in locating its position. ? (3)

11. What are Balmer series? Calculate the wave number of the longest and shortest wavelength transition in the Balmer series of atomic spectrum. (3)

12. (*a*) What observations in scattering experiment led Rutherford to make the following conclusions ?
(*i*) The most of the space in an atom is empty.
(*ii*) The whole of the mass of the atom is present in the centre of the nucleus.
(*iii*) Nucleus has positive charge.
(*b*) What is the value of orbital angular momentum for an electron in 2*s* orbital ?
(*c*) How many electrons in an atom may have $n = 4$ and $m_s = +1/2$?
(*d*) What physical meaning is attributed to the square of the absolute value of wave function Ψ^2? (5)

To check your performance, see HINTS and SOLUTIONS to some questions at the end of Part I of the book.

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UNIT 3

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

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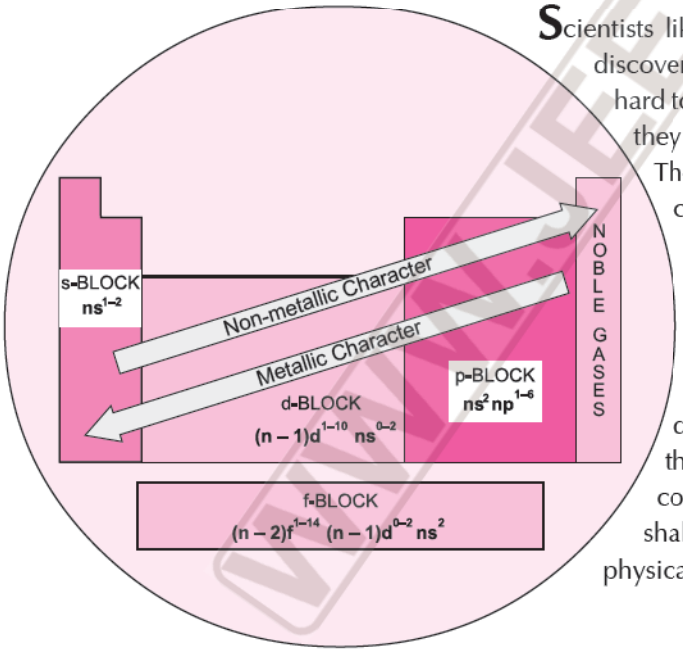

Scientists like to find patterns. About 200 years ago, scientists were discovering lots of new elements. However, they were struggling hard to bring order and pattern to the vast amount of information they were discovering about the elements and their properties. The periodic table is an important triumph for the nineteenth century chemists and has become an important landmark in the history of chemistry. It is used as a sorting system for chemical elements. It has become the everyday support for students and teachers and provides a concise organization of the whole of chemistry.

In the present unit, we will study the historical developments of the periodic table. We will also learn how the periodic classification of elements follows as a logical consequence of the electronic configuration of atoms. We shall also study some of the important periodic trends in the physical and chemical properties of elements.

NEED FOR CLASSIFICATION OF ELEMENTS

Upto the end of seventeenth century, only 31 elements were known. Therefore, it was very easy to study and remember the properties of these elements. However, during the later part of the eighteenth century, the pace of discovery of new elements quickened. Between 1800 to 1869, the number of identified elements had become nearly double to 63. With such a large number of elements, it became difficult to study individually the chemistry of all these elements and their innumerable compounds. At this stage, it was realised that there should be some simple way to study and remember the numerous properties of the elements and their compounds. This gave rise

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to necessity of classification of the elements into various groups having similar properties. This has been done by *arranging the elements in such a way that similar elements are placed together while dissimilar elements are separated from one another.* This is known as **classification of elements.** Such a classification of the elements has resulted in the formulation of the periodic table. **Periodic table** may be defined as

the arrangement of the known elements according to their properties in a tabular form.

At present, about 118 elements are known. Of these, the recently discovered elements are man made. Efforts to synthesize new elements are continuing. The periodic classification of the elements has extremely simplified their study. Not only the periodic classification rationalizes the known chemical facts about elements, but it also helps to predict new ones for undertaking further study.

HISTORICAL DEVELOPMENT OF THE PERIODIC TABLE*

Since the beginning of the nineteenth century, scientists have been trying to find a basis of grouping elements having similar properties. **Lavoisier** classified the elements simply as metals and non-metals. However, this classification proved to be inadequate. Some of the earlier important attempts to classify the elements are briefly summed up below:

1. Dobereiner's triads

In 1817, a German scientist, Johann Dobereiner classified the elements in groups of three elements called **triads.** ***The elements in a triad had similar properties and the atomic weight of the middle member of each triad is very close to the arithmetic mean (average) of the other two elements.*** The common triads of Dobereiner classification were : *lithium, sodium* and *potassium*; *calcium, strontium* and *barium; chlorine, bromine* and *iodine;* etc.

Table 1. Dobereiner's triads

Element	Atomic weight	
Lithium	7	Mean of 1st and 3rd
Sodium	23	$\frac{7+39}{2} = 23$
Potassium	39	
Calcium	40	Mean of 1st and 3rd
Strontium	88	$\frac{40+137}{2} = 88.5$
Barium	137	
Chlorine	35.5	Mean of 1st and 3rd
Bromine	80	$\frac{35.5+127}{2} = 81.25$
Iodine	127	

*Not in the syllabus of CBSE.

For example, in the triad of lithium, sodium and potassium,

Atomic weight of middle element (sodium) = 23

Mean of atomic mass of lithium and potassium

$$= \frac{7+39}{2} = 23.$$

The Dobereiner's relationship was also referred to as **law of triads.** However, it seemed to work only for a few elements. It was dismissed as coincidence because all the known elements could not be arranged in triads.

2. De Chancourtois Classification

The next reported attempt was made by a French geologist, A.E.B.de Chancourtois in 1862. He arranged the then known elements in order of increasing atomic weights and proposed a **cylindrical table of elements** to display the periodic recurrence of properties. He observed that the elements with similar properties fell in a vertical line from the centre of the spiral. However, this did not attract much attention.

3. Newlands law of octaves

In 1865, an English chemist, John Newlands proposed a new system of grouping elements of similar properties. According to him, ***when the elements are arranged in the increasing order of atomic weights, the properties of every eighth element are similar to the first one.*** Newlands called this relation as the **law of octaves** due to similarity with the musical scale.

This relationship is just like every eighth note resembles the first in octaves of music. The Newlands law of octaves seemed to be true only for elements up to calcium as shown below :

Table 2. Newlands's law of octaves

Element	Li	Be	B	C	N	O	F
At. Wt.	7	9	11	12	14	16	19
Element	Na	Mg	Al	Si	P	S	Cl
At. Wt.	23	24	27	29	31	32	35.5
Element	K	Ca					
At. Wt.	39	40					

In the above table, sodium (Na), the eighth element from lithium (Li) is similar to Li and similarly the next eighth element potassium is similar to Na. The same is true for magnesium resembling beryllium, aluminium resembling boron, etc.

4. Lother Meyer's arrangement

In 1869, a German chemist, Lother Meyer used the physical properties such as atomic volume, melting

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point, boiling point, etc., to arrive at his table of elements. He showed that *when the properties of the elements such as atomic volume, melting point, boiling point, etc. are plotted as a function of their atomic weights, the elements with similar properties occupied almost similar positions.* On this basis, Lother Meyer proposed that ***when the elements are arranged in the increasing order of their atomic weights, similarities in physical and chemical properties appear at regular intervals.***

All these attempts provided same clue that there are certain regularities among the elements. The first most successful attempt in classification of elements was made by a Russian chemist Dmitri Mendeleev.

5. Mendeleev's Periodic Law

In 1869, Mendeleev made a remarkable contribution to the classification of elements. On the basis of physical and chemical properties of the elements, he gave a law known as the **periodic law.** The law states that

the physical and chemical properties of elements are periodic function of their atomic weights.

This means that when the elements are arranged in the order of their increasing atomic weights, the elements with similar properties recur at regular intervals. Such orderly recurring properties in a cyclic fashion are said to be occurring ***periodically.*** This is responsible for the name periodic law or periodic table.

Mendeleev's Periodic Table

On the basis of his periodic law, Mendeleev arranged all the known elements in the form of a table known as periodic table. It was observed that the elements with similar properties recur at regular intervals or periodically. As a result of this, the elements fall in certain *groups* or *families.* The elements in each group were similar to each other in many properties. The properties repeated periodically. Mendeleev's periodic table published in 1905 is given in Table 3 ahead. The horizontal rows in the periodic table are called **periods** and the vertical columns are called **groups.**

Mendeleev's system of classifying elements was more elaborate than the earlier attempts. He realized that some of the elements did not fit in very well with his scheme of classification if the order of atomic weight was strictly followed. He showed courage to ignore the order of atomic weights, thinking that the atomic weight measurements might be incorrect. He placed the elements with similar properties together. For example, iodine has lower atomic weight than that of tellurium (of Group VI) but he placed iodine in Group VII alongwith fluorine, chlorine and bromine because of similarities in their properties.

The Mendeleev's classification gave him so much confidence that he boldly left certain spaces or gaps for undiscovered elements. By considering the properties of the adjacent elements in his table, he predicted the properties of the undiscovered elements. Later on, when these elements were discovered, their properties were found to be exactly similar to those predicted by Mendeleev. For example, gallium and germanium were not discovered at that time, when Mendeleev formulated his periodic table and therefore, he left gaps for these elements. He not only predicted the existence of the elements but he estimated their properties. He tentatively named these elements as ***eka-aluminium*** and ***eka-silicon*** (from the Sanskrit word *eka* meaning '*next*') because he believed that these would be similar to aluminium and silicon respectively. When chemists discovered these elements, Mendeleev's prediction of their properties proved to be remarkably correct. Some of the properties predicted by Mendeleev for these elements and those found experimentally are given in Table 4.

Table 4. Comparison of the properties predicted for eka-aluminium and eka-silicon by Mendeleev with those observed for gallium and germanium.

Property	Eka-aluminium predicted by Mendeleev	Gallium (found)	Eka-silicon predicted by Mendeleev	Germanium (found)
Atomic mass	68	70	72	72.6
Density ($g\ cm^{-3}$)	5.9	5.94	5.5	5.36
Melting point (K)	Low	29.78	High	1231
Formula of oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
Formula of chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$

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Table 3. Mendeleev's periodic table published in 1905 showing elements and their atomic weights.

SERIES	GROUPS OF ELEMENTS								
	0	I	II	III	IV	V	VI	VII	VIII
1	—	Hydrogen H 1.008	—	—	—	—	—	—	
2	Helium He 4.0	Lithium Li 7.03	Beryllium Be 9.1	Boron Br 11.0	Carbon C 12.0	Nitrogen N 14.04	Oxygen O 16.00	Fluorine F 19.0	
3	Neon Ne 19.9	Sodium Na 23.5	Magnesium Mg 24.3	Aluminium Al 27.0	Silicon Si 28.4	Phosphorus P 31.0	Sulphur S 31.0	Chlorine Cl 35.45	
4	Argon Ar 38	Potassium K 39.1	Calcium Ca 40.1	Scandium Sc 44.1	Titanium Ti 48.1	Vanadium V 51.4	Chromium Cr 52.1	Manganese Mn 55.0	Iron Fe 55.9 / Cobalt Co 59 / Nickel Ni 59 / (Cu)
5	—	Copper Cu 63.6	Zinc Zn 65.4	Gallium Ga 70.0	Germanium Ge 72.3	Arsenic As 75	Selentium Se 79	Bromine Br 79.95	
6	Krypton Kr 81.8	Rubidium Rb 85.4	Strontium Sr 87.6	Yttrium Y 89.0	Zirconium Zr 90.6	Niobium Nb 94.0	Molybdenum Mo 96.0	—	Ruthenium Ru 101.7 / Rhodium Rh 103.0 / Palladium Pd 106.5 / (Ag)
7	—	Silver Ag 107.9	Cadmium Cd 112.4	Indium In 114.0	Tin Sn 119.0	Antimony Sb 120.0	Tellurium Te 127	Iodine I 127	
8	Xenon Xe 128	Cesium Cs 132.9	Barium Ba 137.4	Lanthanum La 139	Cerium Ce 140				
9									
10		—	—	Ytterbium Yb 173	—	Tantalum Ta 183	Tungsten W 184	—	Osmium Os 191 / Iridium Ir 193 / Platinum Pt 194.9 / (Au)
11		Gold Au 197.2	Mercury Hg 200.0	Thallium Tl 204.1	Lead Pb 206.9	Bismuth Bi 208	—	—	
12	—	—	Radium Ra 224	—	Thorium Th 232	—	Uranium U 239		

Formulae of oxides	R	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
Formulae of hydrides	R	RH	RH_2	RH_3	RH_4	RH_3	RH_2	RH	

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The success of Mendeleev's bold quantitative predictions convinced Chemists of the usefulness of Mendeleev's periodic table and led to its wide acceptance.

Important Contributions of Mendeleev's Periodic Table

Mendeleev's periodic table was one of the greatest achievements in the development of chemistry. Some of the important contributions of his periodic table are :

1. Systematic study of the elements. The Mendeleev's periodic table simplified the study of chemistry of elements. Knowing the properties of one element in a group, the properties of other elements in the group can be easily guessed. Thus, it became very useful in studying and remembering the properties of a large number of elements.

2. Correction of atomic masses. The Mendeleev's periodic table helped in correcting the atomic masses of some elements based on their positions in the table. For example, atomic mass of beryllium was corrected from 13.5 to 9. Similarly, with the help of this table, atomic masses of indium, gold, platinum etc. were corrected.

3. Prediction of new elements. At the time of Mendeleev, only 56 elements were known. While arranging these elements, he left some gaps. These gaps represented the undiscovered elements. Mendeleev predicted the properties of these undiscovered elements on the basis of their positions. For example he predicted the properties of gallium (*eka*-aluminium) and germanium (*eka*-silicon) which were discovered later. The observed properties of these elements were found to be similar to those predicted by Mendeleev (Table 4).

Defects of Mendeleev's Periodic Table

In spite of many advantages, the Mendeleev's periodic table had certain defects also. Some of these are given below :

1. Position of hydrogen. Hydrogen is placed in group I. However, it resembles the elements of group I (alkali metals) as well as the elements of group VIIA (halogens). Therefore, the position of hydrogen in the periodic table is not correctly defined.

2. Anomalous pairs. In certain pairs of elements, the increasing order of atomic masses was not obeyed. In these cases, Mendeleev placed elements according to similarities in their properties and not in increasing order of their atomic masses. For example, argon (Ar, atomic mass 39.9) is placed before potassium (K, atomic mass 39.1). Similarly, cobalt (Co, atomic mass 58.9) is placed before nickel (Ni, atomic mas 58.6) and tellurium (Te, atomic mass 127.6) is placed before iodine (I, atomic mass 126.9). These positions were not justified.

3. Position of isotopes. Isotopes are the atoms of the same element having different atomic masses but same atomic number. Therefore, according to Mendeleev's classification, these should be placed at different places depending upon their atomic masses. For example, isotopes of hydrogen with atomic masses 1, 2 and 3 should be placed at three places. However, isotopes have not been given separate places in the periodic table.

4. Some similar elements are separated and dissimilar elements are grouped together. In the Mendeleev's periodic table, some similar elements were placed in different groups while some dissimilar elements had been grouped together. For example, copper and mercury resembled in their properties but they had been placed in different groups. At the same time, elements of group I A such as Li, Na and K were grouped with copper (Cu), silver (Ag) and gold (Au), though their properties are quite different.

5. Cause of periodicity. Mendeleev did not explain the cause of periodicity among the elements.

6. Position of lanthanoids (or lanthanides) and actinoids (or actinides). The fourteen elements following lanthanum (known as lanthanoids, from atomic number 58–71) and the fourteen elements following actinium (known as actinoids, from atomic number 90—103) have not been given separate places in Mendeleev's table.

In order to cover more elements, Mendeleev modified his periodic table.

ATOMIC NUMBER AND MODERN PERIODIC LAW

In 1913, Moseley, a young English physicist discovered the relationship between X-ray spectra and the atomic number of the elements. When high energy electrons were focused on a target made of the elements under study, X-rays were generated. He studied the frequencies of X-rays emitted from the elements and observed that the frequency (ν) of the prominent X-rays emitted by an element was proportional to the atomic number and not to the atomic weight. He gave a general equation :

$$\sqrt{\nu} = a\,(Z - b)$$

where ν is the frequency of the emitted X-ray and a and b are constants that are same for all the elements. A plot of $\sqrt{\nu}$ versus atomic number (Z) gives a straight line. This led Moseley to conclude **that atomic number and not atomic weight is the fundamental property of the atoms.** He, therefore, suggested that atomic number instead of atomic weight should be the basis of classification of elements.

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The acceptance of atomic number, as the important characteristic of an atom, led to the **modern periodic law. Modern periodic law** may be stated as

the physical and chemical properties of the elements are periodic functions of their atomic numbers.

This law implies that the physical and chemical properties of the elements depend on atomic number and this dependency shows periodicity. Consequently, when the elements are arranged in the order of their increasing atomic numbers, it is observed that the elements of similar properties recur at regular intervals or periodically. As a result of this, the elements fall in certain groups and lead to an arrangement called the periodic table.

With the modern periodic law as the guiding principle and the modern theory of atomic structure, many new forms of the periodic table have been proposed from time to time. Some forms emphasise chemical reactions and valence, whereas other forms stress the electronic configurations of elements. However, the general plan of the table has remained the same as proposed by Mendeleev. Furthermore, it is now recognized that the periodic law is essentially the consequence of the periodic variation in *electronic configurations* of atoms, which determine the physical and chemical properties of the elements and their compounds.

THE LONG FORM OF THE PERIODIC TABLE

The most widely used periodic table these days is '*The Long Form of the Periodic Table*'. This is constructed on the basis of repeating **electronic configuration of the atoms** when the elements are arranged in the order of increasing atomic numbers. Long form of the periodic table is given in Fig. 1 ahead.

Structural Features of the Long Form of the Periodic Table

The long form of the periodic table consists of horizontal rows called **periods** and vertical columns called **groups.** There are altogether **seven periods**. These are numbered as 1, 2, 3, 4, 5, 6 and 7. The first period contains 2 elements and the subsequent periods consist of 8, 8, 18, 18, 32 and 32 elements respectively. Fourteen elements of both sixth and seventh periods (called lanthanoids and actinoids respectively) are placed in separate columns at the bottom of the periodic table.

There are **eighteen groups** in the long form of the periodic table. Earlier, these groups were designated as IA, IB, IIA, IIB.... VIII or zero groups. According to new recommendations of the International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18 (Fig. 1).

These are discussed below :

Periods

A horizontal row in the periodic table is called **period.**

In terms of electronic structure of the atom, a period constitutes a series of elements whose atoms have the same number of electron shells *i.e.* principal quantum number (n). Thus, the period indicates the value of n for the outermost or valence shell of the atom of the element. Each successive period in the periodic table is associated with the filling of the next higher principal energy level (n=1, n=2, n=3, etc.) *There are* **seven periods** *and each period starts with a different principal quantum number.*

It can be seen that the number of elements in each period is twice the number of **atomic orbitals** available in the energy level that is being filled.

Electronic Configurations of Elements in Periods

Elements of First Period

The **first period** corresponding to $n = 1$ is unique because it contains only **two elements.** This is not surprising because first energy shell (K) has only one orbital (*i.e.* 1*s*) which can accommodate only two electrons. This means that there can be only two elements in which one and two electrons are present in first energy level. The first period contains hydrogen ($1s^1$) and helium ($1s^2$).

Elements of Second Period

The **second period** contains **8 elements** because for $n = 2$, there are four orbitals (one 2*s* and three 2*p*) in second energy shell (L). In all, these four orbitals have a capacity of eight electrons and, therefore, second period has **eight elements** in it. It starts with lithium (Z = 3) in which one electron enters the 2*s*-orbital. The period ends with neon (Z = 10) in which the second shell is complete ($2s^2\ 2p^6$).

Elements of Third Period

In **third period** corresponding to $n = 3$, there are nine orbitals : one 3*s*, three 3*p* and five 3*d*. However, we know from energy level diagram for multielectron atoms (Unit 2) that 3*d*-orbitals are higher in energy than 4*s*-orbitals. Consequently, 3*d*-orbitals are filled after filling 4*s*-orbital. Hence, this period involves the filling of only four orbitals (3*s* and 3*p*) and contains **eight elements** from sodium (Z = 11) to argon (Z =18).

Elements of Fourth Period

The **fourth period** corresponding to $n = 4$ involves the filling of one 4*s*-and three 4*p*-orbitals (4*d* and 4*f* orbitals are higher in energy than 5*s*-orbitals

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LONG FORM OF THE PERIODIC TABLE

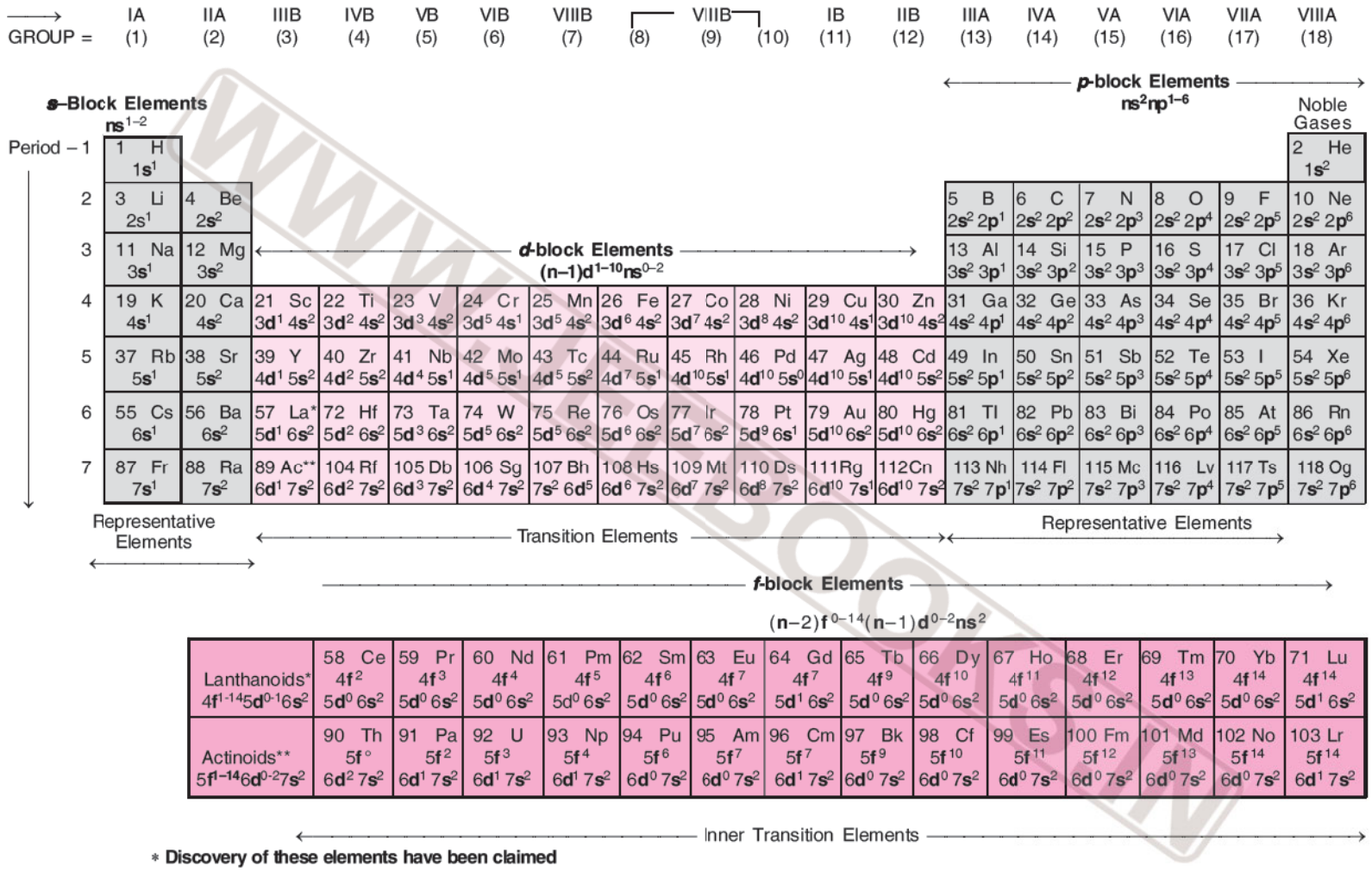

Fig 1. Long form of the periodic table.

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and are filled later). In between 4*s*-and *4p*-orbitals, five 3*d*-orbitals are filled which have energies in between these orbitals. Thus, in all nine orbitals are to be filled and, therefore, there are **eighteen elements** in fourth period from potassium (Z = 19) to krypton (Z = 36). In this period, we come across elements which involve the filling of *3d* orbitals. These are known as ***transition series of elements***. This starts from scandium (Z = 21) which has electronic configuration $3d^1\ 4s^2$ and ends at zinc (Z = 30) with *3d* orbitals completely filled having electronic configuration $3d^{10}\ 4s^2$.

Elements of Fifth Period

The **fifth period,** like the fourth period also consists of 18 elements. It begins with rubidium (Z = 37) with filling of 5*s*-orbital and ends at xenon (Z = 54) with the filling up of the 5*p*-orbitals. This period also contains ten elements of ***4d transition series*** starting at yttrium (Z = 39).

Elements of Sixth Period

The **sixth period** contains 32 elements (Z = 55 to 86) and successive electrons enter into 6*s*, 4*f,* 5*d* and 6*p*-orbitals, in that order. It starts with cesium (Z = 55) and ends at radon (Z = 86). In addition to ten elements of *5d transition series*, this period contains 14 elements which involve filling up of *4f* orbitals beginning from cerium (Z = 58) to lutetium (Z = 71). The series of elements are called **inner transition series or *lanthanoid series***.

Elements of Seventh Period

The **seventh period,** is similar to the sixth period with successive filling up of the *7s, 5f, 6d* and *7p* orbitals and includes most of the man made radio-active elements. This period ends at the element with atomic number 118, which would belong to the noble gas family. Some of the elements of this period have been recently established and named. This period also contains 14 elements which involve the filling of *5f* orbitals starting from actinium (Z = 89). This is also called ***5f–inner transition series*** **or** ***actinoid series***.

This also provides a theoretical justification for periodicity occurring at regular intervals of 2, 8, 8, 18, 18 and 32. These numbers *i.e.,* 2, 8, 18 and 32 are also called **magic numbers.** The number of elements and the corresponding orbitals being filled are given in Table 5.

The first three periods containing 2, 8 and 8 elements respectively are called **short periods,** the next three periods containing 18, 18 and 32 elements respectively are called **long periods.**

Groups

A vertical column in the periodic table is known as **group.**

In terms of electronic structure of the atom, a group constitutes a series of elements whose atoms have the same outermost electronic configurations. There are **18 groups** in the long form of the periodic table. According to the new recommendations of International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18. Previously, these were numbered only from I to VIII as A and B groups. Both the systems of numbering the groups is given in the periodic table. However, the old convention is still used in many books.

The first two groups on the extreme left and last six groups on the extreme right involve the filling of *s*-and *p*-orbitals, respectively. These groups represent the main groups of the periodic table and are numbered as 1, 2, 13, 14, 15, 16, 17 and 18 corresponding to general configurations of ns^1, ns^2, $ns^2\ np^1$, $ns^2\ np^2$, $ns^2\ np^3$, $ns^2\ np^4$, $ns^2\ np^5$, $ns^2\ np^6$, respectively (in the old system these were denoted as IA, IIA, IIIA, IVA, VA, VIA, VIIA and VIIIA (or zero) respectively corresponding to general configurations of ns^1, ns^2, $ns^2\ np^1$,.....$ns^2\ np^6$ respectively. The elements present in these groups are known as **normal** or **representative elements.**

The first three periods containing 2, 8 and 8 electrons involve the filling of only *s*-and *p*-subshells. But the fourth period involves the filling of 3*d*-subshells also and this results into ten more groups. These ten groups lie in between first two and last six groups, (see periodic table) *i.e.,* between group 2 (IIA) and group 13 (IIIA) because 3*d*-orbitals are filled after

Table 5. Number of elements (corresponding to electrons) in each period.

Period (n)		Orbitals being filled up	Number of electrons or elements in the period	
First	(1)	1*s*	2	= 2
Second	(2)	2*s* 2*p*	2 + 6	= 8
Third	(3)	3*s* 3*p*	2 + 6	= 8
Fourth	(4)	4*s* 3*d* 4*p*	2 + 10 + 6	= 18
Fifth	(5)	5*s* 4*d* 5*p*	2 + 10 + 6	= 18
Sixth	(6)	6*s* 4*f* 5*d* 6*p*	2 + 14 + 10 + 6	= 32
Seventh	(7)	7*s* 5*f* 6*d* 7*p*	2 + 14 + 10 + 6	= 32

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4*s*-orbitals but before 4*p*-orbitals. These are numbered from 3 to 12 (in the old system these were usually labelled as **B groups** *i.e.,* **IB, IIB, IIIB,**...etc.). The elements present in these groups are called **transition elements.** *The name is derived from the fact that they represent transition (change) in character from reactive metals (elements of groups 1 and 2) on one side to the non-metals (elements of group 13 to 18) on the other side.*

There are two more rows at the bottom of the periodic table. These rows consist of fourteen elements after lanthanum (Z = 57) and fourteen elements which follow actinium (Z = 89). These are placed separately in the periodic table to save space and avoid undue sidewise expansion of the periodic table. This arrangement also helps in keeping elements with similar properties in a single column. The elements in the first row, starting from cerium are called **lanthanoids (or lanthanides)** and the elements present in the second row starting from thorium are called **actinoids (or actinides).** These lanthanoids and actinoids together are called **inner transition elements** or rare earth metals and these are built up by filling of *f*-orbitals.

NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBER MORE THAN 100

Today, we have elements upto 118. These elements were earlier named traditionally by its discoverer or discoverers. However, in recent years, disputes regarding the original discoveries of some elements of atomic number 104 and above have arisen. This is because the new elements with very high atomic numbers are very unstable and only minute quantities of elements are obtained. This has led to controversy in deciding the claims of more than one scientist for the discovery and names assigned by them for the new element discovered.

For example, both American and Soviet scientists claimed credit for discovery of element 104. The Americans named it ***Rutherfordium*** (symbol **Rf**) while Soviets named it ***Kurchatovium*** (symbol **Ku**). To overcome this problem, the IUPAC in 1997 gave the approved official names for elements with atomic numbers 104 to 109. The IUPAC has also recommended a systematic nomenclature for naming the new elements until their names are officially recognized. This nomenclature is based on the Latin words for their numbers.

The IUPAC Rules for Nomenclature of Elements with Z > 100 are :

(*i*) The name of the element should be derived directly from the atomic number using the numerical roots for their numbers. For example, nil for 0, un for 1, bi for 2, tri for 3 and so on as given in Table 6.

Table 6. Notations for numbers (word root) used by IUPAC Nomenclature of Elements.

Digit	Root Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

(*ii*) The names are derived by combining together the roots in the order of digits which make up the atomic number and ium is added at the end.

(*iii*) In certain cases, the names are shortened. For example, if enn occurs before nil, the second n should be dropped and written as ennil. Similarly, the final i of bi and tri should be dropped when these occur before ium as bi + ium $\Rightarrow$ bium, tri + ium = trium

(*iv*) The symbol of the element is obtained from the first letters of the numerical roots (abbreviations) of the digit which make up the atomic number of the element.

For example, for atomic number 104, the name may be written as :

un (1) + nil (0) + quad (4) + ium $\longrightarrow$ unnilquadium

and is assigned the symbol Unq.

The IUPAC names for the elements with atomic number more than 100 are given in Table 7.

Table 7. Nomenclature of elements with atomic number above 100.

Atomic Number	Name	Symbol	IUPAC official name	IUPAC symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	Nb
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnillium	Uun	Darmstadtium	Ds
111	Unununnium	Uuu	Rontgenium	Rg

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*112	Ununbium	Uub	Copernicium	Cn*
**113	Ununtrium	Uut	Nihonium	Nh
*114	Ununquadium	Uuq	Flerovium	Fl*
**115	Ununpentium	Uup	Moscovium	Mc
*116	Ununhexium	Uuh	Livermorium	Lv*
**117	Ununseptium	Uus	Tennessine	Ts
**118	Ununoctium	Uuo	Oganesson	Og

* The element 112 has been named as copernicium with chemical symbol Cn. It is named in honour of scientist astronomer Nicolaus Copernicus. The element 114 is named Flerovium with chemcial symbol Fl to honour the Flerov Laboratory of Nuclear Reactions and the element 116 is named Livermorium with chemical symbol Lv to honour the Lawrence Livermore National Laboratory.

** Recently, IUPAC have confirmed the discovery of four new elements with atomic numbers 113, 115, 117 and 118 and named them. Therefore, the seventh row of the periodic table is now complete.

DIVISION OF ELEMENTS INTO *s, p, d* AND *f*-BLOCKS

The long form of the periodic table can be divided into four main blocks. These are ***s, p, d* and *f*-blocks.** This division of elements is based upon the electronic configurations of the atoms. In this division, the elements which involve the filling of a particular orbital (*i.e.*, ***s, p, d*** or ***f***) are grouped together as shown in Fig. 2. (These are also shown in Long form of the Periodic Table.

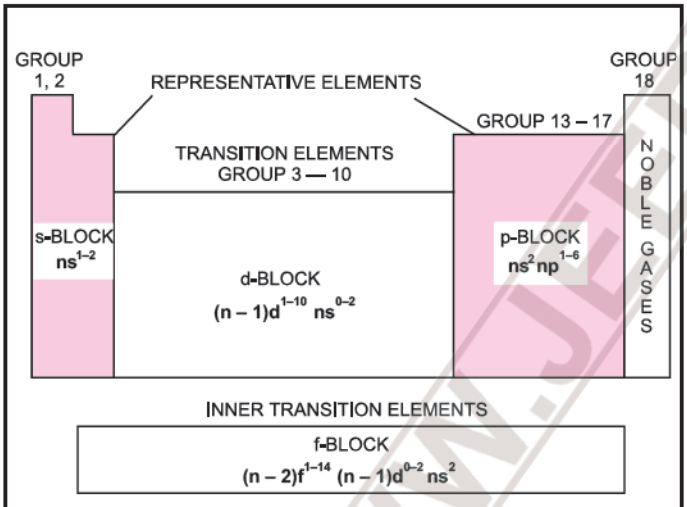

Fig. 2. Division of periodic table into *s, p, d* and *f*-blocks.

(*i*) *s*-block elements

The elements in which the last electron enters the s-orbital of their outermost energy level are called *s*-**block elements.** It consists of elements of groups 1 and 2 having the ground state electronic configurations of outermost shell as ns^1 and ns^2 respectively (where n stands for outermost energy shell). The elements corresponding to ns^1 configuration are called **alkali metals** while those corresponding to ns^2 configuration are called **alkaline earth metals.** Thus, the general electronic configuration of *s*-block elements may be expressed as :

General electronic configuration of s-block elements : ns^{1-2}

General characteristics of *s*-block elements

The general characteristics of *s*-block elements are :

(*i*) They are soft metals having low melting and boiling points.

(*ii*) They have low ionisation enthalpies.

(*iii*) They are very reactive and readily form **univalent** (alkali metals) or **bivalent** (alkaline earth metals) ions by losing one or two valence electrons respectively. Because of their high reactivity, they are never found pure in nature.

(*iv*) They act as strong reducing agents.

(*v*) Most of them impart characteristic colours to the flame.

(*vi*) They mostly form ionic compounds except lithium and beryllium.

(*ii*) *p*-block elements

The elements in which the last electron enters the p-orbital of their outermost energy level are called ***p*-block *elements.*** The elements of groups 13 to 18 involving addition of one ($ns^2\,np^1$), two ($ns^2\,np^2$), three ($ns^2\,np^3$), four ($ns^2\,np^4$), five ($ns^2\,np^5$), and six ($ns^2\,np^6$) electrons respectively in *p*-orbitals and *s*-orbitals are already filled in their atoms constitute *p*-block. The general electronic configuration for the atoms of this block may be written as :

General electronic configuration of p-block elements : $ns^2\,np^{1-6}$

General characteristics of *p*-block elements.

The general characteristics of *p*-block elements are :

(*i*) They include both metals and non-metals. There is a regular gradation from metallic to non-metallic character as we move along a period from left to right in this block. The metallic character increases as we go down the group.

(*ii*) Their ionisation enthalpies are relatively high as compared to *s*-block elements.

(*iii*) They form mostly covalent compounds.

(*iv*) Some of them show more than one oxidation states in their compounds.

(*v*) There occurs a gradation from reducing to oxidising properties as we move across the periods of this block.

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The elements of *s*- and *p*-block are collectively called **representative elements.** The elements of last group (18) having ns^2np^6 configuration are called **noble gases.** All the orbitals in the valence shell of the noble gases are completely filled and they have no tendency to lose or gain electrons. Therefore, the noble gases exhibit very low reactivity. Preceding the noble gas family are two chemically important groups of **non-metals.** These are **halogens** (group 17) and **chalcogens** (group 16). These two groups of elements can readily accept one and two electrons respectively to attain noble gas configurations and form univalent and divalent negative ions. In these elements, the non-metallic character increases as we move from left to right across a period and metallic character increases as we go down the group.

(*iii*) *d*-block elements

The elements in which the last electron enters the d-orbitals of their last but one (called penultimate) energy level constitute ***d*-block elements.** This block consists of the elements lying between *s* and *p* blocks starting from fourth period and onwards. They constitute groups 3 to 12 in the periodic table. In these elements the outermost shell contains one or two electrons in their *s*-orbital (*ns*) but the last electron enters the last but one *d*-subshell *i.e.,* $(n-1)\,d$. The general electronic configuration for the atoms of *d*-block may be written as :

General electronic configuration : $(n-1)\,d^{1-10}\,ns^{0-2}$

Thus, it is the *d*-orbital which is progressively being filled in the elements of this block. These elements are also called **transition elements** because the properties of these elements are midway between those of *s*-block and *p*-block elements. In a way, transition metals form a bridge between the chemically active metals of *s*-block elements and the less active elements of Groups 13 and 14. Therefore, they represent transition (change) in behaviour and take their familiar name "**transition elements**."

The *d*-block comprises three complete rows of ten elements and one incomplete row. These rows are called *first, second* and *third transition series* which involve the filling of 3*d,* 4*d* and 5*d*-orbitals respectively. These series are also called **transition series.**

First transition series

Scandium (Z = 21) to Zinc (Z = 30)

(4th period : 3d-orbitals are gradually filled)

Second transition series

Yttrium (Z = 39) to Cadmium (Z = 48)

(5th period : 4d-orbitals are gradually filled)

Third transition series

Lanthanum (Z = 57), Hafnium (Z = 72) to Mercury (Z = 80)

(6th period : 5d-orbitals are gradually filled)

Fourth transition series

Actinium (Z = 89), Rutherfordium (Z = 104) to Copernicium (Z = 112)

(7th period : 6*d*-orbitals are gradually filled)

General characteristics of *d*-block elements. The general characteristics of *d*-block elements are :

(i) They are metals having high melting and boiling points.

(ii) Most of them form coloured compounds.

(iii) They have a good tendency to form complex compounds.

(iv) Their compounds are generally paramagnetic.

(v) They exhibit several oxidation states.

(vi) Most of the transition elements such as Mn, Ni, Co, Cr, V, Pt and their compounds are used as catalysts.

(*iv*) *f*-block elements

The elements in which the last electron enters the f-orbitals of their atoms are called ***f*-block elements.** In these elements, the last electron is added to the third to the outermost (called antipenultimate) energy level; $(n-2)\,f$. These consist of two series of elements placed at the bottom of the periodic table :

(i) The first series follows lanthanum, La (Z=57) and the elements present in this series ($_{58}$Ce – $_{71}$Lu) are called **lanthanoids** or **lanthanides.** These are also called **rare earth elements.**

(ii) The second series follows actinium, Ac (Z = 89) and the elements present in this series ($_{90}$Th – $_{103}$Lr) are called **actinoids** or **actinides.** These are of radioactive nature.

The general electronic configuration of *f*-block elements may be written as :

General electronic configuration :
$(n-2)\,f^{1-14}\,(n-1)\,d^{0-2}\,ns^2$

For example, for **lanthanoids**, the general electronic configuration is $4f^{1-14}\,5d^{0-1}\,6s^2$ while for **actinoids**, it is $5f^{1-14}\,6d^{0-2}\,7s^2$.

The elements included in these two series are called **inner transition elements,** *because they form transition series within the transition elements of d-block.*

General characteristics of *f*-block elements

The general characteristics of *f*-block elements are :

(i) They are heavy metals.

(ii) They generally have high melting and boiling points.

(iii) They exhibit variable oxidation states.

(iv) They form coloured ions.

(v) They have the tendency to form complex compounds.

(vi) Actinoids are radioactive in nature. Many of the actinoid elements have been made only in nano gram quantities or even less by nuclear reactions

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and their chemistry is not fully studied. The elements after uranium are called ***transuranium elements***.

On the basis of above four blocks, the elements can be classified into the following four general types :

Classification of Elements into four General Types

1. Noble gases. The noble gases are found at the end of each period in group 18. Except for helium, the elements have completely filled *s*- and *p*-orbitals of the outermost shell *i.e.*, $ns^2\ np^6$. Helium has $1s^2$ configuration. All these elements are highly stable and chemically inert under ordinary conditions.

2. Representative elements (*s* and *p*-block elements). All the elements of *s* and *p*-block with exception of noble gases are called representative elements. They represent two groups 1 (alkali metals) and 2 (alkaline earth metals) on the extreme left and five groups from group 13 to 17 on the right hand side of the periodic table.

3. Transition elements. The elements of *d*-block elements are called transition elements. These include elements of group 3 to 12 lying in between the representative elements (between *s* and *p*-blocks).

4. Inner transition elements. The elements of *f*-block are called inner transition elements. These comprise two series of 14 elements called **lanthanoids** and **actinoids.**

Classification as Metals and Non-metals

In addition to classifying the elements into *s*-, *p*-, *d*- and *f*–block, the elements can be classified on the basis of their properties as :

(i) *Metals* and (ii) *Non-metals*

Metals comprise more than 78% of all known elements and appear on the **left hand side** of the Periodic Table. They have high melting and boiling points and are generally solid at room temperature (mercury is an exception which is a liquid at room temperature). Gallium and caesium also have very low melting points, 303 K and 302 K respectively. They are good conductors of heat and electricity. They are malleable (can be flattened into thin sheets) and ductile (can be drawn into wires). They have bright lustre.

On the other hand, non-metals are present on the ***right hand side*** of the periodic table. They are usually solids or gases at room temperature with low melting and boiling points (boron and carbon are exceptions). *The only liquid non-metal is bromine*. Most non-metals are brittle and are neither malleable nor ductile.

In general, the elements become more metallic as we go down a group and non-metallic character increases as we move from left to right across a period in the Periodic Table. It may be noted that the change from metallic to non-metallic character is not abrupt as shown by zig-zag line in Fig 3 ahead. The elements bordering this line (silicon, germanium, asenic, antimony, tellurium, etc.) show properties characteristic of both metals and non-metals. These are called **metalloids** or **semimetals.**

Advantages of the Long Form of the Periodic Table

The important **advantages** of the long form of the periodic table are given below :

(i) This classification is based on the atomic number which is a more fundamental property of the elements.

(ii) Since this classification is based on the atomic number and not on the atomic mass, the position of placing isotopes at one place is fully justified.

(iii) The position of elements in the periodic table is governed by the electronic configurations, which determine their properties.

(iv) It is easy to remember and reproduce.

(v) The systematic grouping of elements into four blocks; *s, p, d* and *f* has made the study of the elements more simple.

(vi) The position of some elements which were misfit on the basis of atomic mass is now justified on the basis of atomic number. For example, argon proceeds potassium because argon has atomic number 18 and potassium has 19.

(vii) The lanthanoids and actinoids which have properties different from other groups are placed separately at the bottom of the periodic table.

Defects of the Long Form of the Periodic Table

Although the Long Form of the periodic table has helped in systemising the study of chemistry of elements, yet it has certain defects. The **main defects** of this table are :

(i) The position of hydrogen is not settled. It resembles with alkali metals as well as halogens.

(ii) Lanthanoids and actinoids have not been accommodated in the main body of the periodic table.

Prediction of Period, Group and Block of an Element

The period, group or block of an element can be predicted from the **electronic configuration** of the elements.

1. **Period of the element corresponds to the principal quantum number of the valence shell.**
2. **Block of the element corresponds to the subshell which receives the last electron.**

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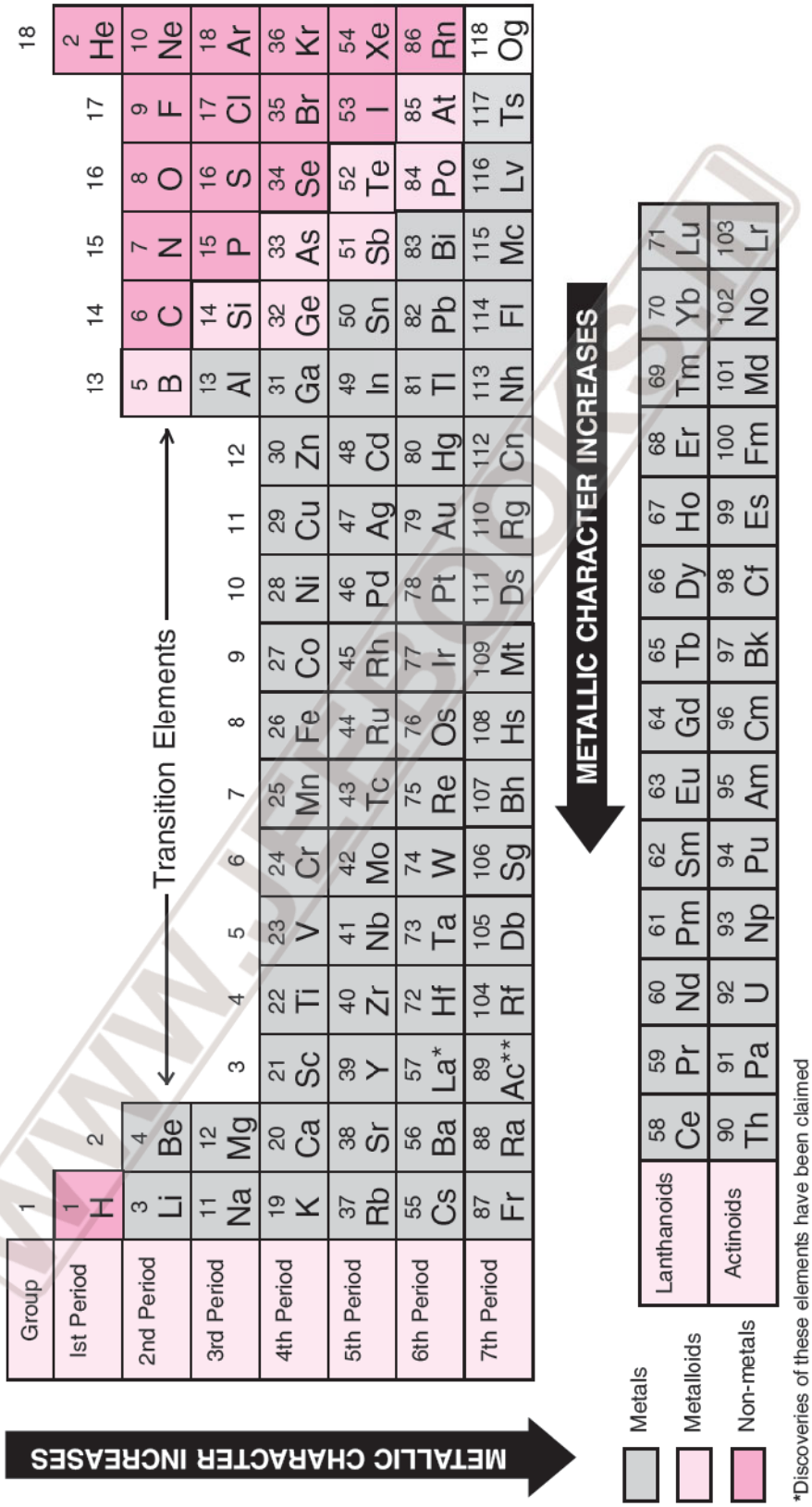

Fig 3. Position of metals, non-metals and metalloids in the periodic table.

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3. Group is predicted from the number of electrons in the outermost shell or penultimate (last but one, *i.e.*, *n*–1) shell as follows :

For *s-block element*, group number is equal to *number of valence electrons (ns electrons).*

For *p-block element*, group number is equal to *10 + number of valence electrons (ns and np).*

For *d-block element*, group number is equal to total *number of electrons in (n–1) d and ns subshells.*

SOLVED EXAMPLES

Example 1.

What would be the IUPAC name and symbol of the element with atomic number 120 ? **N.C.E.R.T.**

Solution: The roots for 1, 2 and 0 are un, bi and nil respectively.

∴ Name of element : Unbinilium

Symbol : Ubn

Example 2.

How would you justify the presence of 18 elements in the 5th period of the periodic table ? **N.C.E.R.T.**

Solution: The 5th period involves the filling of 5th shell (n=5). This period has 4*d*, 5*s* and 5*p* available orbitals. The total number of available orbitals are 9 and therefore the maximum number of electrons that can be accommodated is 18. Thus, 5th period contains 18 elements.

Example 3.

The elements Z = 107, 108 and Z = 109 have been made recently. Indicate the group in which you will place the above elements. **N.C.E.R.T.**

Solution: The electronic configurations of these elements are :

Z = 107 [Rn] $5f^{14}\,6d^5\,7s^2$

Z = 108 [Rn] $5f^{14}\,6d^6\,7s^2$

Z = 109 [Rn] $5f^{14}\,6d^7\,7s^2$

These elements will be placed in *d*-block in groups 7th, 8th and 9th respectively.

Example 4.

Arrange the following elements in the increasing order of metallic character : **N.C.E.R.T.**

Si, Be, Mg, Na, P.

Solution: We know that metallic character increases down a group and decreases along a period as we move from left to right.

Hence the order of increasing metallic character is P < Si < Be < Mg < Na.

Example 5.

Predict the position of the element in the periodic table satisfying the electronic configuration $(n\text{-}1)d^1ns^2$ *for n = 4* **N.C.E.R.T.**

Solution: For n = 4, the electronic configuration is $3d^14s^2$. The element belongs to *d*-block elements.

Group number = No. of electrons in $(n-1)d$ subshell + No. of electrons in nth shell

= 1 + 2 = 3

Example 6.

(a) Elements A, B, C and D have atomic numbers 12, 19, 29 and 36 respectively. On the basis of electronic configuration, write to which group of the periodic table each element belongs.

(b) Predict the blocks to which these elements can be classified. Also predict their periods and groups.

(c) Which of these are representative elements ?

Solution: *(a)*

Element	At. No.	Electronic configuration	Group
A	12	$1s^2\,2s^2\,2p^6\,3s^2$	2
B	19	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$	1
C	29	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$	11
D	36	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6$	18

[According to old system, these elements belong to groups : IIA (A), IA (B), IB (C), VIIIA or zero (D)]

(b) Prediction of blocks

(i) A receives the last electron in 3*s*-subshell, therefore, it belongs to ***s*-block.**

Period = 3rd

Group = No. of valence electrons = **2**

(ii) B receives the last electron in 4*s*-orbital, therefore, it belongs to ***s*-block.**

Period = 4th

Group = No. of valence electrons = **1**

(iii) C receives the last electron in 3*d*-orbital, therefore, it belongs to ***d*-block.**

Period = 4th

Group = No. of electrons in *ns* and $(n-1)$ *d* subshells = **11**

(iv) D receives the last electron in the 4*p*-orbital, therefore, it belongs to ***p*-block.**

Period = 4th

Group = 10 + valence electrons = 10 + 8 = **18**

(c) The elements A and B are **representative elements.**

Example 7.

The electronic configurations of some elements are given below :

(i) $1s^2\,2s^2\,2p^6\,3s^1$

(ii) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^1$

(iii) $1s^2\,2s^2\,2p^3$

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(*iv*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

(*v*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

(*vi*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

(*vii*) $1s^2\ 2s^2\ 2p^6$

(*viii*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

Name the elements. Out of these which

1. *is an alkaline earth metal* **2.** *has lowest chemical reactivity* **3.** *belong to group 15 of the periodic table* **4.** *is a transition element* **5.** *is halogen* **6.** *belong to p-block* **7.** *belong to second period.*

Solution:

Names of elements:

(*i*) Sodium (Na) (*ii*) Scandium (Sc)
(*iii*) Nitrogen (N) (*iv*) Calcium (Ca)
(*v*) Chlorine (Cl) (*vi*) Phosphorus (P)
(*vii*) Neon (Ne) (*viii*) Sulphur (S).

1. Calcium (iv) is an alkaline earth metal.
2. Neon (*vii*) has lowest chemical reactivity.
3. Nitrogen (*iii*) and phosphorus (*vi*) belong to group 15 of the periodic table.
4. Scandium (*ii*) is a transition element.
5. Chlorine (*v*) is halogen.
6. Nitrogen (*iii*), chlorine (*v*), phosphorus (*vi*), neon (*vii*) and sulphur (***viii***) belong to *p*-block.
7. Nitrogen (*iii*) and neon (*vii*) belong to second period of the periodic table.

❑ **Example 8.**

Element A, B, C, D and E have the following electronic configurations :

A : $1s^2 2s^2 2p^1$

B : $1s^2 2s^2 2p^6 3s^2 3p^1$

C : $1s^2 2s^2 2p^6 3s^2 3p^3$

D : $1s^2 2s^2 2p^6 3s^2 3p^5$

E : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Which among these will belong to the same group in the periodic table ?

Solution: We know that the elements having similar valence electronic configuration belong to the same group of the periodic table. Therefore, elements A and B having three electrons in the valence shell belong to the same group *i.e.,* group 13 of the periodic table.

Practice Problems

◑ **1.** Write the name and deduce the atomic numbers of the following atoms :

(*i*) The third alkali metal.

(*ii*) Second transition element.

(*iii*) The fourth noble gas.

(*iv*) Fourth element in the second period.

◑ **2.** The outer electronic configurations of some elements are :

(*i*) $3s^2\ 3p^4$ (*ii*) $3d^{10}\ 4s^2$

(*iii*) $3s^2\ 3p^6\ 4s^2$ (*iv*) $6s^2\ 4f^3$

State to which block in the periodic table each of these elements belong.

◑ **3.** How many elements are present in the third period of the *p*-block elements ?

◑ **4.** Complete the following statements :

(a) There are.....periods in the long form of the periodic table.

(b) The *s* block element having highest atomic mass is.....

(c) The elements Cu, Ag and Au are called .....metals.

◑ **5.** An element X belongs to the third period of the *p*-block elements. It has 4 electrons in the outermost shell. Name the element.

◑ **6.** Which family of elements has the electronic configuration $ns^2\ np^4$?

◑ **7.** The element 118 has not yet been discovered. What is its IUPAC name and symbol ?

◑ **8.** Arrange the following elements in the increasing order of metallic character :

B, Al, Mg, K.

◑ **9.** Arrange the following elements in the increasing order of non-metallic character :

B, C, Si, N and F.

◑ **10.** Rn (Z = 86) is the last noble gas discovered. Predict what will be the atomic number of the next noble gas to be discovered. Write its symbol.

Answers to Practice Problems

◐ **1.** (*i*), K, 19 (*ii*) Ti, 22 (*iii*) Kr, 36 (*iv*) C, 6.

◐ **2.** (*i*) *p* (*ii*) *d* (*iii*) *s* (*iv*) *f*.

◐ **3.** Six.

◐ **4.** (*a*) 7 (*b*) Ra (*c*) Coinage.

◐ **5.** Silicon.

◐ **6.** Oxygen family. This family is also called chalcogens.

◐ **7.** Ununoctium, Uuo

◐ **8.** B < Al < Mg < K

◐ **9.** F < N < Si < C < B

◐ **10.** Atomic number of next noble gas to be discovered will be 118. Symbol : Uuo

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add on

Conceptual Questions 1

Q.1. On the basis of quantum numbers, justify that the sixth period of the periodic table should have 32 elements. ***N.C.E.R.T.***

Ans. The sixth period of the periodic table begins with n=6. It involves the filling of *6s, 4f, 5d* and *6p* subshell in the increasing order of energy. The total number of orbitals available are 16 and therefore, the maximum number of electrons that can be accommodated is 32. Thus, the sixth period of the periodic table should have 32 elements.

Q.2. In terms of period and group where would you locate the element with Z = 114 ? ***N.C.E.R.T.***

Ans. The electronic configuration of the element with Z=114 would be [Rn] $5f^{14}\ 6d^{10}\ 7s^2\ 7p^2$. Since it has n=7 for the valence shell, it belongs to **7th period**. It receives the last electron in p-orbital. Therefore, it belongs to p-block. The group number will be 10 + 4 (No. of electrons in ns and np orbitals) **= 14**

So, it belongs to 7th period and 14th group.

Q.3. The elements Z = 117 and 118 have been recently discovered and named. In which family group would you place these elements and also give electronic configuration in each case. Name these elements.

Ans. The electronic configuration of the element with Z = 117 would be [Rn] $4f^{14}\ 5d^{10}\ 7s^2\ 7p^5$.

It has outermost ns^2np^5 configuration and therefore, it belongs to **halogen family** or **Group 17**.

IUPAC name: Tennessine, Ts

The electronic configuration of the element with Z=118 would be [Rn] $4f^{14}\ 5d^{10}\ 7s^2\ 7p^6$. It has outermost ns^2np^6 configuration and therefore, belongs to noble gases or group 18. IUPAC name: Oganesson, Og.

Q.4. Write the atomic number of the element present in the third period and sixteenth group of the periodic table. Give its name.

Ans. Since it belongs to 3rd period, it will have outershell as n = 3. Its configuration would be [Ne] $3s^2\ 3p^4$. So its atomic number **= 16.** It is sulphur.

Q.5. Give the general electronic configurations of

(*i*) *p*-block **(*ii*) actinoids**

Ans. (*i*) ns^2np^{1-6} (*ii*) $5f^{1-14}\ 6d^{0-2}\ 7s^2$

Q.6. An element 'X' with atomic number 112 has been recently predicted. Its electronic configuration is : [Rn] $5f^{14}\ 6d^{10}\ 7s^2$. Predict

(*i*) group and (*ii*) block in which this element would be placed (*iii*) IUPAC name and symbol.

Ans. The configuration of the element is :

$$[Rn]\,5f^{14}\,6d^{10}\,7s^2$$

(*i*) It belongs to 12th group. (*ii*) It belongs to *d* block. (*iii*) IUPAC name is : Copernicium; Symbol : Cn.

Q.7. The element 119 has not been discovered so far. What would be the IUPAC name and the symbol for this element? On the basis of periodic table, predict the electronic configuration of this element and the formula of its most stable chloride and oxide. ***(NCERT Exemplar Problem)***

Ans.

IUPAC name	:	Ununennium
Symbol	:	Uue
Electronic	:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$
configuration		$4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 5f^{14}\ 6s^2\ 6p^6\ 6d^{10}\ 7s^2\ 7p^6\ 8s^1$ or [At] $8s^1$
Formula	:	Chloride : ACl
	:	Oxide : A_2O

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Q.8. Eka-aluminium and eka-silicon were named given by Mendeleev for the then unknown elements gallium and germanium respectively. A recently discovered element has first named as eka-mercury. What is its atomic number? Write its group number, electronic configuration, IUPAC name, official name and symbol.

Ans. The element which comes after mercury in the periodic table is eka-mercury. Its atomic number = 80 + 32 = 112
Electronic configuration: [Rn] $5f^{14}\,6d^{10}\,7s^2$

IUPAC name : Uub

Official name: Copernicium, symbol : Cn

Q.9. Write the IUPAC names, official names and symbols for the elements having atomic numbers 108, 114 and 116.

Ans.

Z	=	108	Unniloctium	Uno	;	Hassium	Hs
Z	=	114	Ununquadium	Uuq	;	Flerovium	Fl
Z	=	116	Ununhexium	Uuh	;	Livermorium	Lv

CAUSES OF PERIODICITY

The recurrence of similar properties of the elements after certain regular intervals when they are arranged in the order of increasing atomic numbers is called periodicity.

The classification of the elements in certain families was based upon the observed similarities in the physical and chemical properties. But, *why do certain elements exhibit similar properties and why do the similar properties recur at regular intervals of atomic numbers,* were some important questions yet to be answered.

We know that an atom consists of a nucleus surrounded by electrons. In ordinary chemical reactions, the nuclei of the atoms do not undergo any change and, therefore, it is the distribution of the electrons in the various shells of their atoms that determine the physical and chemical properties of the elements. Further, it has been also found that the properties of atoms do not depend so much on the arrangement of electrons in the inner shells. Thus, it must primarily be the arrangement of electrons in the outermost shell (called the valence shell) that determines the properties of the atoms. For example, the electronic configurations of the atoms of alkali metals group (Table 8) shows that they all have one electron in the *s*-orbital of the outermost valence shell preceded by the noble gas configuration ($ns^2\ np^6$, but for Li, ns^2). The general electronic configuration of these may be written as (noble gas) ns^1 : where *n* stands for principal quantum number.

Table 8. Electronic configurations of alkali metals.

Element	At. No.	Electronic configuration
Li	3	$1s^2\mathbf{2s^1}$
Na	11	$1s^2 2s^2\,2p^6\,\mathbf{3s^1}$
K	19	$1s^2 2s^2\,2p^6\,3s^2\,3p^6\,\mathbf{4s^1}$
Rb	37	$1s^2 2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,\mathbf{5s^1}$
Cs	55	$1s^2 2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,5s^2 5p^6\,\mathbf{6s^1}$
Fr	87	$1s^2 2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,5s^2 5p^6\,6s^2\,4f^{14}\,5d^{10}\,6p^6\,\mathbf{7s^1}$

Thus, the **cause of periodicity of the properties of elements is**

the repetition of similar electronic configuration of their atoms in the outermost energy shell (or valence shell) after certain regular intervals.

For example, all the alkali metals have a great tendency to lose the single electron in order to acquire a stable noble gas configuration. Consequently, all of them are very reactive metals.

Similarly, all the members of the halogen family have two electrons in the *s*-orbital and five electrons in the *p*-orbital of the valence shell (Table 9). The general electronic configuration of halogens may be expressed as $ns^2\ np^5$.

Table 9. Electronic configurations of halogens.

Element	At. No.	Electronic configuration
F	9	$1s^2\mathbf{2s^2\,2p^5}$
Cl	17	$1s^2 2s^2\,2p^6\,\mathbf{3s^2\,3p^5}$
Br	35	$1s^2 2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,\mathbf{4s^2\,4p^5}$
I	53	$1s^2 2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,\mathbf{5s^2 5p^5}$

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This configuration reveals that each of these halogens has a natural tendency to gain one electron to acquire stable noble gas configuration. Thus, all the halogens form halide ion, X^-, readily in their compounds.

PERIODIC TRENDS IN PROPERTIES OF ELEMENTS

There are numerous physical properties of elements such as melting points, boiling points, enthalpy of fusion, enthalpy of vaporization, enthalpy of atomization, density, etc. which show periodic variations. These are indirectly related to electronic configurations of atoms. However, some physical properties such as atomic size, ionization enthalpy, electron gain enthalpy, electronegativity, valency, etc. are directly related to the electronic configuration of atoms. Let us discuss some of the important properties and their **periodic trends.**

ATOMIC RADIUS

The size of atom is very important property because many physical and chemical properties are related to it. If the atom is assumed to be spherical, the atomic size is given by the radius of the sphere and is called atomic radius. Generally, the term **atomic radius** means ***the distance from the centre of the nucleus to the outermost shell of electrons***. However, it is difficult to determine the exact radius of the atom because of the following reasons :

(i) The size of an atom is (approximately 1.2Å or 1.2×10^{-10} m in radius) very small.

(ii) According to the probability picture of electrons, an atom does not have well defined boundary. The probability of finding the electron is never zero even at large distances from the nucleus.

(iii) It is not possible to isolate an atom and measure its radius. The atomic radius of an atom is also affected by the presence of other atoms in its neighbourhood. Therefore, the size of atom may change in going from one set of environment of another.

(iv) Size of atom also changes from one bonded state to another.

Thus, we can only arbitrarily define atomic radius as the **effective size** which means *the distance of closest approach of one atom to another atom in a given bonding situation*. The approximate radii of atoms can be determined by measuring the distance between the centres of two neighbouring atoms (called internuclear distance) in a covalent molecule by X-ray diffraction, electron diffraction or other spectroscopic techniques.

As shown in Fig. 4., this internuclear distance corresponds to twice the radius of an atom and, therefore, half of this distance gives the atomic radius.

Atomic radii may be assigned different names such as **covalent or metallic** depending upon the type of bonding between the atoms.

Covalent Radius

It may be defined as ***one half of the distance between the nuclei of two covalently bonded atoms of the same element in a molecule.***

For homonuclear molecule,

$$r_{covalent} = \frac{\text{Internuclear distance between two bonded atoms}}{2}$$

For example, as shown in Fig. 4., the internuclear distance between two hydrogen atoms in H_2 molecule is 74 pm.

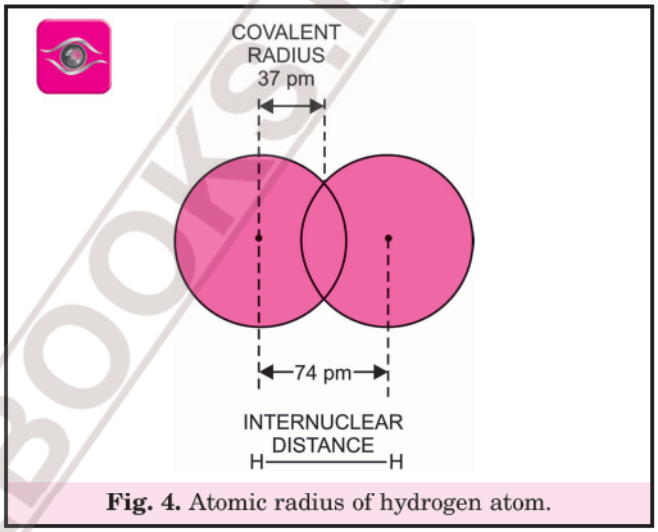

Fig. 4. Atomic radius of hydrogen atom.

$\therefore$ Atomic radius of hydrogen $= \frac{74}{2} = 37$ pm.

Similarly, the atomic radii of chlorine and bromine are 99 pm and 114 pm because the internuclear distances in chlorine Cl—Cl and Br—Br are 198 pm and 228 pm respectively.

In the case of molecules containing different atoms (heteronuclear molecules), the **covalent radius** of an atom may be defined as :

the distance between the centre of nucleus of the atom and the mean position of the shared pair of electrons between the bonded atoms.

It has been observed that when the covalent radii for different atoms joined by a single covalent bond are added, the resulting value agrees fairly well with the experimentally determined internuclear distance of that molecule.

Metallic Radius

In case of metals, a large number of atoms are closely packed and are held together by means of metallic bonds. The close packing of the metal atoms is known as metallic lattice. The **metallic radius is taken as**

one half of the internuclear distance between the two neighbouring atoms of a metal in a metallic lattice.

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For example, the distance between two adjacent copper atoms in metallic copper is 256 pm. Therefore, metallic radius of copper is 256/2 *i.e.*, 128 pm.

Thus, the covalent radius gives the size of a non-metallic element when the atoms are bound together by a single covalent bond in a covalent molecule. For metals, the metallic radius gives the size of a metallic element in metals held by metallic bonds.

It may be noted that for simplicity, *we may use the term atomic radius for both covalent or metallic radius depending on whether the element is a non-metal or a metal*. However, covalent radii or metallic radii are always shorter than the atomic radii in the uncombined atoms. This is so because the covalent bond is formed by the overlapping of atomic orbitals and the overlap region becomes common between the two atoms.

Variation of Atomic Radii in the Periodic Table

The following periodic trends in atomic radii have been observed.

(*a*) Variation in a period. In general, *the atomic radii decrease with increase in atomic number (going from left to right) in a period.*

For example, in the second period, the atomic radii decrease from Li to Ne through Be, B, C, N, O and F as given in Table 10. The variation of atomic radius with atomic number in a second period is also shown in Fig. 5.

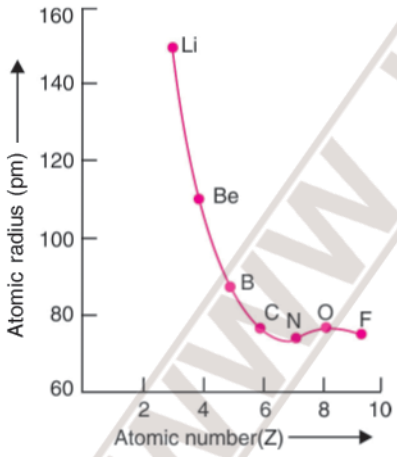

Fig. 5. Variation of atomic radius with atomic number across the second period.

This may be explained on the basis of increasing nuclear charge along a period. With the increase in atomic number from lithium to fluorine, the magnitude of the nuclear charge increases progressively by one unit while the corresponding addition of electron takes place in the same principal shell (second). Since, the electrons in the same shell *do not screen each other from the nucleus,* the increase in nuclear charge is not neutralised by the extra valence electron. As a result, electrons are pulled closer to the nucleus by the increased effective nuclear charge and thereby, cause a decrease in the size of the atom. In this way, the atomic size goes on decreasing across the period.

It may be noted from Fig. 5 and Table 10 that in second period atomic size decreases from Li to N. After nitrogen atomic size i.ncreases for oxygen and then decreases for fluorine. This anomalous behaviour of oxygen and fluorine may be explained as follows.

In nitrogen, all the three 2*p*-orbitals have one electron each; $2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$. When we move from nitrogen to oxygen, the nuclear charge increases by one. But at the same time, one of the 2*p*-orbital has two electrons in oxygen; $2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$. The electrons in same orbital repel each other. *In case of oxygen, the interelectronic repulsions outweigh the effect of increased nuclear charge so that the atomic size increases from N to O.* On further moving from O to F, there is increase in nuclear charge by one and at the same time two, 2*p* orbitals have two electrons each, which repel each other. However, *in case of fluorine, the increased nuclear charge outweighs the effect of interelectronic repulsions and hence the size decreases from O to F.* It may be noted that both O and F have size larger than N. Thus, the anomalous behavior of O and F is due to the combined effect of increased nuclear charge and interelectronic repulsions.

Table 10. Decrease in atomic radii in second period.

Element and its atomic number	$_3$Li	$_4$Be	$_5$B	$_6$C	$_7$N	$_8$O	$_9$F	$_{10}$Ne
Nuclear charge	+3	+4	+5	+6	+7	+8	+9	+10
Outer electronic configuration	$2s^1$	$2s^2$	$2s^22p^1$	$2s^22p^2$	$2s^22p^3$	$2s^22p^4$	$2s^22p^5$	$2s^22p^6$
Atomic radius (pm)	152	111	88	77	70	74	72	160*

* It is inert gas radius or van der Waals radius.

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Similarly, for the third period, the atomic radii decrease as given in Table 11.

Table 11. Decrease in atomic radii in third period.

Element and its atomic no.	$_{11}Na$	$_{12}Mg$	$_{13}Al$	$_{14}Si$	$_{15}P$	$_{16}S$	$_{17}Cl$
Atomic radius (pm)	186	160	143	118	110	104	99

Thus, it may be **concluded** that in general (except for noble gases)

- the alkali metals which are at the extreme left of the periodic table have the largest size in a period.
- the halogens which are present at the extreme right of the periodic table have the smallest size in the period.
- the atomic size **decreases** along the period from left to right.

(*b*) Variation in a group. *The atomic radii of elements increase from top to bottom in a group.* In moving down a group, the nuclear charge is increasing with increase in atomic number and we expect that the size of atom should decrease. However, while going from one atom to another, there is increase in the principal quantum level, although the number of electrons in the outermost shell remains the same. The effect of increase in the size of the electron cloud is more pronounced than the effect of increased nuclear charge. Consequently, the distance of the outermost electron from the nucleus gradually increases down a group. In other words, the size of the atom goes on increasing as we move down a group.

The variation in atomic radius for the members of the alkali metals group (group 1) and halogens group (group 17) are given in Table 12 and are graphically represented in Fig. 6.

Table 12. Atomic radii (pm) in the groups.

Group 1		Group 17	
Element	**Atomic radius**	**Element**	**Atomic radius**
Li	152	F	72
Na	186	Cl	99
K	231	Br	114
Rb	244	I	133
Cs	262	At	140

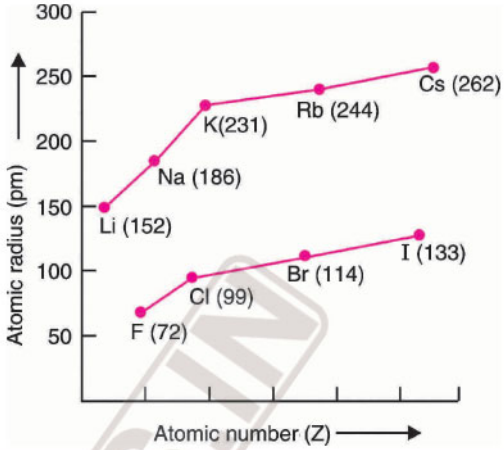

Fig. 6. Variation of atomic radius with atomic number for alkali metals and halogens.

Van der Waals Radius

We observe from Table 12, that atomic radius abruptly increases in case of noble gas element, Ne. This is because of the reason that the values for other elements are for covalent radii while the value of Ne is not covalent radius because neon cannot form neon (Ne_2) molecule. In case of noble gas elements, we measure van der Waals radius because these atoms are held together by weak van der Waals forces in solid state. Like covalent radius, van der Waals radius may also be defined as :

one half of the internuclear distance between the nuclei of two adjacent atoms of the substance belonging to two neighbouring molecules in the solid state.

For example, the internuclear distance between adjacent chlorine atoms in the solid state is 360 pm or 3.6Å as shown in Fig. 7. Therefore, van der Waals radius of chlorine = $\frac{360}{2}$ = 180 pm or 1.80Å.

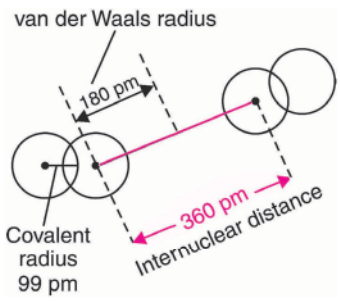

Fig. 7. Van der Waals radius of chlorine.

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Similarly, the internuclear distance between two adjacent hydrogen atoms of two neighbouring molecules in the solid state is 240 pm. Therefore, its van der Waals radius is 240/2 = 120 pm or 1.2Å.

It may be noted that inert gases (except Xe and Kr) donot form chemical compounds and therefore, their atomic radii are usually expressed in terms of van der Waals radii. These are also called **inert gas radii**.

The van der Waals forces existing between atoms in the solid state are weak and the atoms are held at larger distances. Therefore, the internuclear distances in case of atoms held by van der Waals forces are larger than that between covalently bonded atoms. Consquently, **van der Waals radii are always larger than covalent radii.**

Variation of van der Waals radii. Like covalent radii, van der Waals radii also **decrease as we move from left to right in a period** and **increase as we move down the group.** For example,

- van der Waals radii of N, O and F decrease in the period:

N	O	F
150 pm	140 pm	135 pm

- van der Waals radii increase down the group:

F	Cl	Br	I
135 pm	180 pm	195 pm	215 pm

- van der Waals radii of noble gases also increase down the group:

He	Ne	Ar	Kr	Xe
120 pm	160 pm	191 pm	200 pm	220pm

Ionic Radius

The ionic radii correspond to the radii of ions in ionic crystals. The ions are formed as a result of addition or removal of electrons from the outermost shells of atoms. The ions formed by the loss of electrons acquire positive charge and are called **cations** while the ions formed by gain of electrons, get negative charge and are called **anions. Ionic radius** may be defined as

the effective distance from the centre of the nucleus of the ion upto which it has an influence in the ionic bond.

The X-ray studies give the distance between the nuclei of adjacent positive and negative ions in the crystal. If the ions are regarded as spheres, the internuclear distance may be taken equal to the sum of the radius of the cation and the radius of the anion. For example, the internuclear distance of Na^+Cl^- is 276 pm which corresponds to the sum of the ionic radii of Na^+ and Cl^- ions. But the problem of assigning different values to constituting ions is not simple. Unless the value of any one of the ions is known, we cannot calculate the radius of other ion.

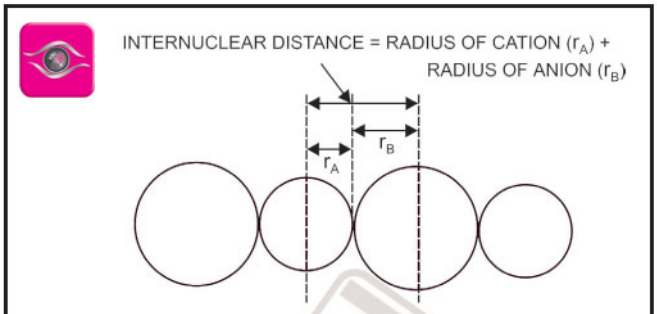

Fig. 8. Internuclear distance and ionic radii.

Several methods have been proposed to fix the absolute value of atleast one ion (the details of these methods are beyond the scope of the present chapter). The radii of all other ions can easily be calculated by subtracting the value of ionic radius of known ion from measured internuclear distance in its compound. Out of the various methods, Pauling's method is the most widely accepted and the values given here are on the basis of this method.

The study of ionic radii leads to two important generalizations :

(i) The radius of positive ion (cation) is always smaller than that of the parent atom.

(ii) The radius of negative ion (anion) is larger than that of the parent atom.

(i) **The radius of cation is smaller than that of the atom.** A cation is formed by the loss of one or more electrons from the gaseous atom. Generally, the whole of the outermost shell of electrons is removed so that the resulting cation is smaller in size. For example, in sodium atom, there is only one electron in the outermost 3*s*-subshell. As sodium atom changes to Na^+ ion, the outermost 3*s*-subshell disappears completely. This disappearance of outermost 3*s*-subshell results in a decrease in size, and therefore, cation is smaller than the atom from which it is formed. It has been observed that the size of Na atom is 186 pm whereas that of corresponding Na^+ ion is only 95 pm.

$$\underset{1s^2\,2s^2\,2p^6\,3s^1}{\underset{(186\ pm)}{Na}} \longrightarrow \underset{(1s^2\,2s^2\,2p^6)}{\underset{(95\ pm)}{Na^+ + e^-}}$$

Similarly, in the formation of Mg^{2+} ion, both the outermost electrons of magnesium atom are lost and thus, Mg^{2+} ion is smaller in size than Mg atom.

$$\underset{(1s^2\,2s^2\,2p^6\,3s^2)}{\underset{(160\ pm)}{Mg}} \longrightarrow \underset{(1s^2\,2s^2\,2p^6)}{\underset{(72\ pm)}{Mg^{2+} + 2e^-}}$$

Moreover, with the removal of electrons from an atom the magnitude of the nuclear charge remains same while the number of electrons decreases. For example, in the formation of sodium ion from sodium atom, the nuclear charge remains + 11 while the number of electrons decreases from 11 to 10.

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	Na	$\xrightarrow{-e^-}$	Na^+
	Atom		Cation
Electrons	11		10
Nuclear charge	+ 11		+ 11
Size	186 pm		95 pm

As a result, the same nuclear charge now acts on less number of electrons. In other words, ***the effective nuclear charge per electron increases and the electrons are more strongly attracted and are pulled towards the nucleus. This causes a decrease in the size of the ion.***

Table 13 illustrates the comparative size of certain atoms and the positive ions formed from them.

Table 13. Atomic and cationic radii of atoms (in pm).

Li	Na	K	Be	Mg	Ca	A1
152	186	231	111	160	197	143
Li^+	Na^+	K^+	Be^{2+}	Mg^{2+}	Ca^{2+}	$A1^{3+}$
60	95	133	39	72	100	50

(*ii*) **The negative ion is always larger than that of the corresponding atom.** The negative ion is formed by the gain of one or more electrons in the neutral atom and the number of electrons increases while the magnitude of nuclear charge remains same. Therefore, the size of an anion will be larger than that of the parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge. For example, in the formation of Cl^- ion from Cl atom, the number of electrons increases from 17 to 18 while the nuclear charge remains same (+17).

	Cl	$\xrightarrow{+e^-}$	Cl^-
	Atom		Anion
Electrons	17		18
Nuclear charge	+ 17		+ 17
Size	99 pm		181 pm

As a result, the same nuclear change acts on larger number of electrons than were present in the neutral atom. In other words, ***effective nuclear charge per electron is reduced and the electron cloud is held less tightly by the nucleus. This causes increase in the size of the ion.***

Thus, as shown in Table 14, the anions are larger in size than the corresponding atoms.

Table 14. Covalent and ionic radii of some atoms (in pm).

Cl	Br	I	O	N
99	114	133	74	75
Cl^-	Br^-	I^-	O^{2-}	N^{3-}
181	196	220	142	171

Variation of Ionic Radii in a Group

The ionic radii in a particular group increase in moving from top to bottom. The reason for the increase is the increase in the principal quantum level though the number of electrons in the valence shell remains the same (similar to those discussed in case of atomic radii). For example, the ionic radii of alkali metal ions increase from Li^+ to Cs^+.

Table 15. Ionic radii of alkali metal ions.

Ion	Ionic radius (pm)
Li^+	60
Na^+	95
K^+	133
Rb^+	149
Cs^+	170

Variation of Size in an Isoelectronic Series

Isoelectronic ions *are ions of different elements which have same number of electrons but differ from one another in magnitude of the nuclear charge.* A set of species having the same number of electrons is known as **isoelectronic series.** One such type of series is shown below in which all the species have ten electrons. As we move from one ion to another the nuclear charge increases and therefore, the force of attraction by the nucleus on the outermost electrons also increases. Consequently, the electrons are pulled more and more strongly and thus size decreases.

Variation of ionic radii in an isoelectronic series*.

Ions	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}
Nuclear charge	+7	+8	+9	+11	+12	+13
Radius (pm)	171	140	136	95	72	50

* All ions have 10 electrons.

Thus, the ionic radii in the the above isoelectronic series decreases as :

$$Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$$

SOLVED EXAMPLES

❑ **Example 9.**

(a) What do you understand by isoelectronic species? Give the formula of a species that will be isoelectronic with the following atoms or ions :

(i) F^- *(ii) Ar*

(iii) Mg^{2+} *(iv)* Rb^+ ***N.C.E.R.T.***

(b) Which of the following species are isoelectronic ?

(i) O^{2-} *(ii)* Mg^{2+} *(iii) Na (iv) F*

(v) Cl^- *(vi)* Al^{3+} *(vii) Ne (viii)* S^{2-}

(ix) Ca^{2+} *(x) K*

Solution: (*a*) Isoelectronic species are those which have same number of electrons.

(i) $F^-(10e^-) : O^{2-}$ *(ii)* $Ar\ (18e^-) : Cl^-$

(iii) $Mg^{2+}\ (10e^-) : Na^+$ *(iv)* $Rb^+\ (36e^-) : Kr$

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(*b*) The number of electrons in these species are :

	Atom/ion	No. of electrons
(*i*)	O^{2-}	8 + 2 = 10
(*ii*)	Mg^{2+}	12 – 2 = 10
(*iii*)	Na	= 11
(*iv*)	F	= 9
(*v*)	Cl^-	17 + 1 = 18
(*vi*)	Al^{3+}	13 – 3 = 10
(*vii*)	Ne	= 10
(*viii*)	S^{2-}	16 + 2 = 18
(*ix*)	Ca^{2+}	20 – 2 = 18
(*x*)	K	= 19

Thus, O^{2-}, Mg^{2+}, Al^{3+} and Ne are isoelectronic and Cl^-, S^{2-} and Ca^{2+} are isoelectronic.

❑ Example 10.

Which of the following species will have the largest and the smallest size?

Mg, Mg^{2+}, Al, Al^{3+} **N.C.E.R.T.**

Solution: Atomic radii decrease across a period. So, Mg will have larger size than Al. Cations are smaller than their parent atoms. So size is : Mg^{2+} < Mg and Al^{3+} < Al. Now, among isoelectronic ions, the ion with the larger positive nuclear charge will have a smaller radius *i.e.,* size is : Al^{3+} < Al.

Hence, the largest species is Mg
the smallest species is Al^{3+}

❑ Example 11.

Which of the following atoms and ions are isoelectronic ?

(i) Al^{3+} *(ii) F (iii)* Cl^-
(iv) O^{2-} *(v) Na (vi)* Mg^{2+}

Arrange the isoelectronic ions in the decreasing order of their size.

Solution: The number of electrons in these atoms or ions are :

Ion or atom	Al^{3+}	F	Cl^-	O^{2-}	Na	Mg^{2+}
No. of Electrons	10	9	18	10	11	10

Thus Al^{3+}, O^{2-} and Mg^{2+} are isoelectronic ions because all the three ions have ten electrons. Now nuclear charge in Al^{3+} is + 13, in O^{2-} is +8 and in Mg^{2+} is + 12. With increase in nuclear charge (electrons remain same), size will decrease. Consequently, the size follows the order :

$$O^{2-} > Mg^{2+} > Al^{3+}$$

❑ Example 12.

Arrange the following ions in the order of increasing size :

Be^{2+}, Cl^-, S^{2-}, Na^+, Mg^{2+}, Br^-

Solution: $Be^{2+} < Mg^{2+} < Na^+ < Cl^- < S^{2-} < Br^-$

❑ Example 13.

In each of the following pairs, which species has a larger size ?

(i) Br or Br^- (ii) O^{2-} or F^- (iii) K or K^+ (iv) Li^+ or Na^+ (v) P or As (vi) Na^+ or Mg^{2+}.

Solution: *(i)* Br^- *(ii)* O^{2-} *(iii)* K *(iv)* Na^+ *(v)* As *(vi)* Na^+

Practice Problems

11. Arrange the following in order of increasing radii :
(i) I, I^+, I^- *(ii)* N, O, P *(iii)* F, Cl, Br

12. For each of the following pairs, state which one is large in size :
(a) Li, F *(b)* O, Se *(c)* Fe^{2+}, Fe^{3+} *(d)* Br, Br^-
(e) Na^+, F^- *(f)* K, K^+

13. Account for the difference in size of Na^+ [0.095 nm] and Mg^{2+} [0.065] both of which have the same noble gas configuration.

14. Arrange each pair of ions in order of increasing ionic radius :
(a) Mg^{2+} and Al^{3+} (b) O^{2-} and S^{2-} (c) O^{2-} and F^-

15. A boy has reported the radii of Cu, Cu^+ and Cu^{2+} as 0.096 nm, 0.122 nm and 0.072 nm respectively. However, it has been noticed that he interchanged the values by mistake. Assign the correct values to different species.

16. Arrange the following ions in the order of increasing size :
Be^{2+}, Cl^-, S^{2-}, Na^+, Mg^{2+}, Br^- **N.C.E.R.T.**

17. Select from each group the species which has the smallest radius:
(a) O, O^-, O^{2-} (b) K^+, Sr^{2+}, Ar (c) Si, P, Cl.

Answers to Practice Problems

11. *(i)* $I^+ < I < I^-$ *(ii)* O < N < P *(iii)* F < Cl < Br.
12. *(a)* Li *(b)* Se *(c)* Fe^{2+} *(d)* Br^- *(e)* F^- *(f)* K.
13. The nuclear charge in Mg^{2+} is more and therefore, its electrons are more strongly attracted.
14. *(a)* $Al^{3+} < Mg^{2+}$ *(b)* $O^{2-} < S^{2-}$ *(c)* $F^- < O^{2-}$
15. Cu [0.122 nm], Cu^+ 0.096 nm Cu^{2+} [0.072 nm].
16. Be^{2+}, Mg^{2+}, Na^+, Cl^-, S^{2-}, Br^-.
17. *(a)* O *(b)* K^+ *(c)* Cl.

IONIZATION ENTHALPY

The electrons in an atom are attracted by the positively charged nucleus. In order to remove an electron from an atom, energy has to be supplied. The quantitative measure of the tendency of an atom to lose an electron is given by **ionization enthalpy.** It is defined as :

the energy required to remove most loosely bound electron from an isolated gaseous atom of the element in its ground state.

Ionization enthalpy is also known as **ionization potential** because *it is the minimum potential difference (in discharge tube) required to remove the most loosely bound electron from an isolated gaseous atom to form gaseous cation.*

The ionization enthalpy is expressed in units of kJ mol^{-1} or electron volt (eV) per atom or k cal mol^{-1}.

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1 eV per atom = 96.49 kJ mol^{-1}

or = 23.06 k cal mol^{-1}

Successive Ionization Enthalpies

The atom may not only lose one electron but can lose more than one electrons also. It may be noted that if the gaseous atom is to lose more than one electron, these are removed one after the other. The *energies required* to remove subsequent electrons from an atom in the gaseous state are known as **successive ionization enthalpies**.

Thus, the first ionization enthalpy, IE_1 is the energy required to remove the most loosely bound electron of the neutral atom and the second ionization enthalpy, IE_2 is the energy required to remove the second electron from the resulting positive ion and so on. Thus, first *ionization enthalpy* of an element (X) may be defined as the enthalpy change ($\Delta_i H$) for the reaction represented as :

$$X(g) \longrightarrow X^+(g) + e^-(g)$$

In other words, **first ionization enthalpy** is the **enthalpy change when most loosely bound electron is removed from an isolated gaseous atom**.

Similarly, we can define **second ionization enthalpy** as ***the energy required or enthalpy change to remove the second most loosely bound electron.*** In other words, it is the enthalpy change for the reaction :

$$X^+(g) \longrightarrow X^{2+}(g) + e^-(g)$$

Since energy is required to remove electrons from an atom and therefore, ionization enthalpies are always **positive.**

Thus, the ionization enthalpy gives the ease with which electron can be removed from an atom. Evidently, ***the smaller the value of ionization enthalpy, the easier it is to remove the electron from the atom.***

Factors Governing Ionization Enthalpy

The magnitude of ionization enthalpy for an atom depends upon the following factors :

1. Size of the atom. *The ionization enthalpy decreases with increase in size of an atom.* This is because the attractive force between the electron and the nucleus is inversely proportional to the distance between them*. Consequently, as the size of the atom increases, the outermost electrons are less tightly held by the nucleus. As a result, *it becomes easier to remove the electron and therefore, ionization enthalpy decreases with increase in atomic size.*

2. Charge on the nucleus. *The ionization enthalpy increases with increase in nuclear charge.* This is because the attractive force between the nucleus and the electron increases with the increase in nuclear charge. The force of attraction is directly proportional to the product of charges on the nucleus and the electron. Therefore, *with the increase in nuclear charge, it becomes more difficult to remove an electron and ionization enthalpy increases.*

3. Screening effect of the inner electrons. *The ionization enthalpy decreases with increase in screening effect of the inner electrons.* In multielectron atoms, the outermost electrons are *shielded or screened* from the nucleus by the inner electrons. This is known as **shielding** or **screening effect.** As a result of this, the outermost electron does not feel the full charge of the nucleus. The actual charge felt by an electron is termed as **effective nuclear charge.** Therefore, the effective nuclear charge (Z_{eff}) is

(Z_{eff}) = Total nuclear charge (Z) – Screening constant (s)

where screening constant takes into account the screening effect of the inner electrons. If the number of electrons in the inner shell is large, the screening effect will be large. As a result, the nuclear electron attraction will be less. Consequently, ionization enthalpy will decrease.

4. Penetration effect of electrons. *The ionization enthalpy increases with increase in penetration power of the electrons.* It is well known that in case of multielectron atoms, the electrons in the *s*-orbital have the maximum probability of being found near the nucleus and this probability goes on decreasing in case of *p, d* and *f*-orbitals. In other words, *s*-electrons are more penetrating towards the nucleus than *p*-electrons and the penetration power decreases in a given shell (same value of *n*) in the order

$$s > p > d > f$$

Now, if the penetration power of the electron is more, it will be closer to the nucleus and will be held firmly. Consequently, ionization energy will be high. Thus, *for the same shell, the ionization enthalpy would be more to remove a s-electron than the energy required to remove a p-electron, which in turn will be more than that for the removal of a d-electron and so on.*

5. Electronic arrangement. The ionization enthalpy also depends upon the electronic configuration of the atom. It has been observed that certain electronic configurations are more stable than others. For example, *half-filled and completely-filled shells have extra stability associated with them.* Consequently, it is difficult to remove electron from these stable

* According to Coulomb's law, the force of attraction F, between the charged particles is given by $F = K \frac{q_1 \times q_2}{r^2}$, where q_1 and q_2 are the charges and r is the distance between them.

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configurations and ionization enthalpy is high. This may be illustrated by the following examples :

(i) The noble gases have the most stable electronic configurations ($ns^2\ np^6$) in each period and therefore, have high ionization enthalpies.

(ii) The elements like Be ($1s^2\ 2s^2$) and Mg ($1s^2\ 2s^2\ 2p^6\ 3s^2$) have completely filled orbitals and their ionization enthalpies are large.

(iii) The elements like N ($1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$) and P ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$) have the configurations in which the orbitals of same subshell are exactly half-filled and are also stable. Hence, they need large energy to remove the electron *i.e.,* their ionization enthalpies are high.

Thus, the more stable the electronic configuration, the greater is the ionization enthalpy.

Variation of Ionization Enthalpy in the Periodic Table

Ionization enthalpy provides another example for understanding periodicity among the elements. The ionization enthalpies of some elements are given in Table 16.

The variation of first ionization enthalpy of elements with atomic number (up to atomic number 60) is shown in Fig. 9.

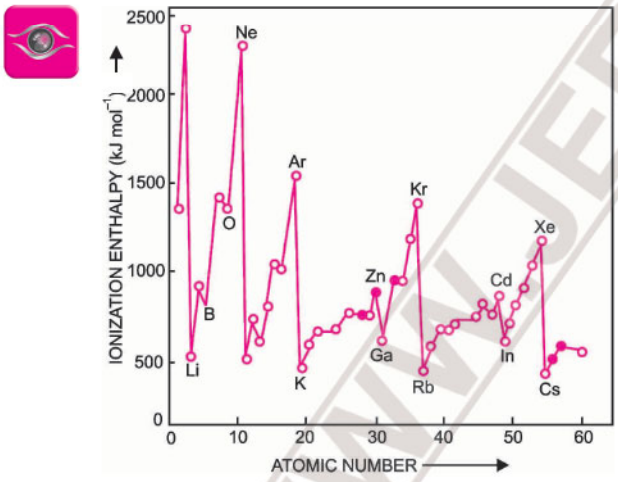

Fig. 9. Variation of ionization enthalpy with atomic number.

It can be seen that in each period, the maxima are found at the noble gases while minima are found at alkali metals. Thus, the metals of group-I with one electron in outermost *s*-orbital are easy to ionise while the noble gases (group 18) with $ns^2\ np^6$ configuration are the most difficult to ionise. The following periodic trends have been observed :

(*a*) Variation along a period. In general, *the ionization enthalpy increases with increasing atomic number in a period.* This is quite clear from the values of ionization enthalpy of the second period elements as given in Fig. 10.

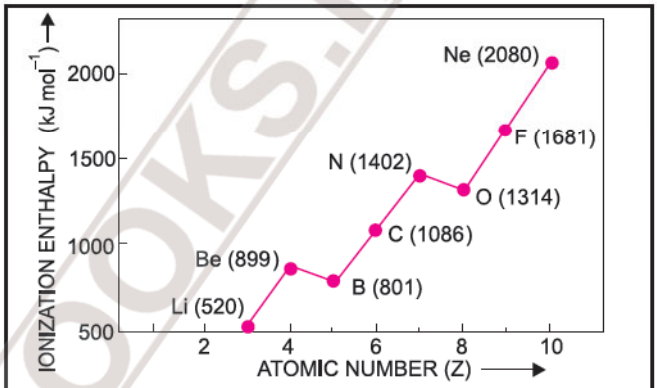

Fig. 10. Variation of ionization enthalpy with atomic number in second period.

The general increase along a period can be explained on the basis of *atomic size and nuclear charge.* We know that

(i) on moving across a period from left to right, the nuclear charge increases.

(ii) the atomic size decreases along a period though the main energy level remains the same.

As a consequence of increased nuclear charge and simultaneous decrease in atomic size, the valence electrons are more and more tightly held by the nucleus. Therefore, more and more energy is needed to remove the electron and hence, ionization enthalpy keeps on increasing.

However, some irregularities in the general trend have been noticed. *These are due to half-filled and completely-filled configurations which have extra stability.* To illustrate this, let us consider the variation

Table 16. Ionization enthalpies of some elements (kJ mol^{-1}).

H							He
1312							2372
Li	Be	B	C	N	O	F	Ne
520	899	801	1086	1402	1314	1681	2080
Na	Mg	Al	Si	P	S	Cl	Br
496	737	577	786	1011	999	1255	1520
K	Ca	Ga	Ge	As	Se	Br	Kr
419	590	579	760	946	941	1143	1350
Rb	Sr	In	Sn	Sb	Te	I	Xe
403	549	558	708	884	869	1009	1170
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
374	502	589	716	703	813	917	1037

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of ionization enthalpy in second period going from one element to another.

Li to Be. On moving from Li to Be, there is an increase in ionization enthalpy and this is due to increased nuclear charge and smaller atomic size.

Be to B. Although the nuclear charge of B is more than Be, yet there is slight decrease in ionization enthalpy from Be to B. This is due to the fact that

(*i*) the electronic configuration of B ($1s^2\ 2s^2\ 2p^1$) is less stable than that of Be ($1s^2\ 2s^2$) which has completely-filled orbitals.

(*ii*) When we consider the same principal quantum shell, an *s*-electron is attracted to the nucleus more than a *p*-electron. In Be, the electron removed during ionization is a 2*s*-electron whereas the electron removed during ionization of B is a 2*p*-electron. Thus we know that the penetration of a 2*s*-electron to the nucleus is more than that of a 2*p*-electron and therefore, 2*p* electron of boron is more shielded from the inner core of electrons than the 2*s* electron of Be. Hence, it is easier to remove the 2*p* electron from B compared to the removal of a 2*s* electron of Be. Thus, B has smaller ionization enthalpy than Be.

As a result the 2*p*-electron of B is not tightly held by the nucleus as 2*s*-electron of Be and hence ionization enthalpy of B is less than that of Be.

B to C to N. As we move from B to C to N, ionization enthalpy keeps on increasing due to increasing nuclear charge and decreasing atomic size.

N to O. Oxygen, the element next to nitrogen has slightly smaller ionization enthalpy as compared to that of nitrogen. It is due to the fact that the electronic configuration of nitrogen atom ($1s^2, 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$), in which 2*p*-orbital is half-filled, is more stable than that of oxygen ($1s^2, 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$). Therefore, ionisation enthalpy of nitrogen is more than that of oxygen.

O to F to Ne. The ionization energy increases from O to F to Ne because of the increased nuclear charge and decrease in size. Neon, the noble gas has the maximum ionization enthalpy in the period due to the stable ($ns^2\ np^6$) electronic configuration.

Similar variation in ionization enthalpy of the elements of third period has also been observed.

(b) **Variation down a group.** *Within a group, there is a gradual decrease in ionization enthalpy in moving from top to bottom.* This is clear from the ionization energy values of the elements of the first group as shown in Fig. 11.

The decrease in ionization enthalpy down a group can be explained in terms of net effect of the following factors :

(*i*) In going from top to bottom in a group, the nuclear charge increases.

(*ii*) There is a gradual increase in atomic size due to an additional main energy shell (*n*).

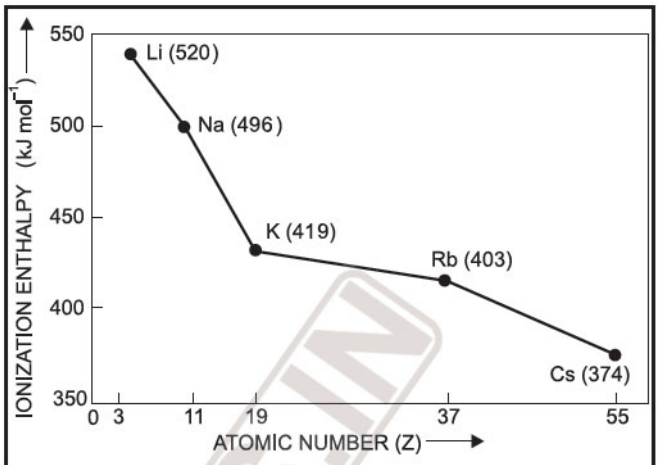

Fig. 11. The variation of ionization enthalpy with atomic number in group 1 (alkali metals) of the periodic table.

(*iii*) There is increase in shielding effect on the outermost electron due to increase in the number of inner electrons.

The effect of increase in atomic size and the shielding effect is much more than the effect of increase in nuclear charge. As a result, the electron becomes less and less firmly held to the nucleus as we move down the group. Hence, there is a gradual decrease in the ionization enthalpies in a group.

Variation in Successive Ionization Enthalpies

The energies required to remove subsequent electrons from the atom in the gaseous state, are known as **succesive ionization enthalpies.** The term first, second, third. ..... ionisation enthalpy refers to the removal of first, second, third.....electron respectively. These changes may be represented as follows :

$$M(g) \xrightarrow{IE_1} M^+(g) + e^-$$
$$M^+(g) \xrightarrow{IE_2} M^{2+}(g) + e^-$$
$$M^{2+}(g) \xrightarrow{IE_3} M^{3+}(g) + e^-$$

Here , IE_1, IE_2 and IE_3 represent first, second and third ionization enthalpies respectively. For example,

$$Li(g) \longrightarrow Li^+(g) + e^- \quad IE_1 = 520\ kJ\ mol^{-1}$$
$$Li^+(g) \longrightarrow Li^{2+}(g) + e^- \quad IE_2 = 7298\ kJ\ mol^{-1}$$

Similarly, the successive ionization enthalpies of aluminium are :

$$Al(g) \longrightarrow Al^+(g) + e^- \quad IE_1 = 577\ kJ\ mol^{-1}$$
$$Al^+(g) \longrightarrow Al^{2+}(g) + e^- \quad IE_2 = 1795\ kJ\ mol^{-1}$$
$$Al^{2+}(g) \longrightarrow Al^{3+}(g) + e^- \quad IE_3 = 2758\ kJ\ mol^{-1}$$

Successive ionization enthalpies are higher

As can be seen, the second ionization enthalpies are higher than the first ionization enthalpies. This is mainly due to the fact that after the removal of the first electron, the atom changes into monovalent positive ion. In the ion, the number of electrons decreases but the nuclear

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charge remains the same. As a result of this, the remaining electrons are held more tightly by the nucleus and it becomes difficult to remove the second electron. Hence, the value of second ionization enthalpy (IE_2) is greater than that of the first (IE_1).

In the same way, the removal of the second electron will result in the formation of dipositive ion and attraction between the nucleus and remaining electrons increases further. This results into higher value of third ionization enthalpy (IE_3) than second (IE_2). The successive ionization enthalpies of some elements of first and second period are given in Table 17.

Successive ionization enthalpy and electronic configurations

The comparison of successive ionization enthalpies of Li and Be gives very interesting results. It can be seen from the successive ionization enthalpies of Li and Be that the first ionization enthalpy (IE_1) of Li is smaller than for Be while the second ionization enthalpy (IE_2) of Li is much greater than for Be. Why is it so, is an important question? This can be easily understood in terms of the electronic configurations of atoms and ions as explained below :

	IE_1	IE_2
Li	520 kJ mol^{-1}	7298 kJ mol^{-1}
Be	899 kJ mol^{-1}	1758 kJ mol^{-1}

The electronic configuration of Li is $1s^2\ 2s^1$ and that of Be is $1s^2\ 2s^2$. Since the configuration of Be is more stable (being completely-filled) than of Li, the IE_1 of Be is more than IE_1 of Li. After the loss of an electron from Li atom, it acquires the electronic configuration of noble gas *i.e.*, $1s^2$. On the other hand, in case of Be atom, the electronic configuration becomes $1s^2\ 2s^1$ after the loss of one electron. Thus, the electronic configuration of Li^+ is more stable than Be^+ and, therefore, IE_2 of lithium is much greater than IE_2 for beryllium.

$$Li\ (1s^2\ 2s^1) \xrightarrow{IE_1} Li^+\ (1s^2) \xrightarrow{IE_2} Li^{2+}\ (1s^1)$$

$$Be\ (1s^2\ 2s^2) \xrightarrow{IE_1} Be^+\ (1s^2\ 2s^1) \xrightarrow{IE_2} Be^{2+}\ (1s^2)$$

The IE_3 of beryllium is also very high because the third electron is to be removed from stable configuration ($1s^2$).

Table. 17. Successive ionization enthalpies of some elements (kJ mol^{-1}).

Element	Electronic configuration	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7	IE_8
H	$1s^1$	1312	–	–	–	–	–	–	–
He	$1s^2$	2372	–	–	–	–	–	–	–
Li	$1s^2 2s^1$	520	7298	11810	–	–	–	–	–
Be	$1s^2 2s^2$	899	1758	14850	21000	–	–	–	–
B	$1s^2 2s^2 2p^1$	801	2427	3638	25024	32824	–	–	–
C	$1s^2 2s^2 2p^2$	1086	2352	4619	6220	37820	47280	–	–
N	$1s^2 2s^2 2p^3$	1402	2858	4576	7473	9443	53255	64328	–
O	$1s^2 2s^2 2p^4$	1314	3388	5296	7468	10987	13323	15160	84054
F	$1s^2 2s^2 2p^5$	1681	3375	6045	8408	11020	15160	17864	92012
Ne	$1s^2 2s^2 2p^6$	2080	3962	6226	9361	12186	15236	–	–

SOLVED EXAMPLES

❑ **Example 14.**

How much energy in joules must be needed to convert all the atoms of sodium to sodium ions present in 2.3 mg of sodium vapours? Ionization enthalpy of sodium is 495 kJ mol^{-1} (At. mass of Na = 23).

Solution: According to the definition of ionisation enthalpy,

$$Na\ (g) + IE \longrightarrow Na^+\ (g) + e^-\ (g)$$

I.E. = 495 kJ mol^{-1}

The amount of energy needed to ionize 1 mole of sodium vapours = 495 kJ mol^{-1}

Moles of sodium vapours present in given sample

$$= \frac{2.3 \times 10^{-3}}{23} = 1 \times 10^{-4}\ \text{mol}$$

$\therefore$ Amount of energy needed to ionize 1×10^{-4} mol of sodium vapours

$= 495 \times 1 \times 10^{-4}$

$= 0.0495$ kJ or 49.5 J

❑ **Example 15.**

Which of the following pairs of elements would you expect to have lower ionization enthalpy? Explain. ***N.C.E.R.T.***

(i) Cl or F *(ii) Cl or S*

(iii) K or Ar *(iv) Kr or Xe*

Solution:

(i) **Cl** is expected to have lower first ionization enthalpy than F because the ionization enthalpy decreases down the group.

(ii) **S** is expected to have lower ionization enthalpy than Cl because ionization enthalpy increases along a period from left to right.

(iii) **K** is expected to have lower ionization enthalpy as compared to Ar. The high value of ionization enthalpy of Ar is due to its completely filled configuration.

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(iv) **Xe** is expected to have lower ionization enthalpy because ionization enthalpy decreases down the group and Xe lies below Kr.

❑ **Example 16.**

The first ionization enthalpy ($\Delta_i H$) values of the third period elements, Na, Mg, and Si are respectively 496, 737 and 786 kJ mol^{-1}. Predict whether the first $\Delta_i H$ value for Al will be more close to 575 or 760 kJ mol^{-1} respectively. Justiy your answer. **N.C.E.R.T.**

Solution:

It will be more close to 575 kJ mol^{-1} because the value of Al should be lower than that of Mg. This is due to effective shielding of 3*p* electrons from the nucleus by 3*s*-electrons.

❑ **Example 17.**

From each set, choose the atom which has the largest ionization enthalpy :

(a) F, O, N (b) Mg, P, Ar (c) B, Al, Ga

Solution:

(*a*) F (*b*) Ar (*c*) B

Practice Problems

◑ **18.** The electronic configurations for some neutral atoms are given below :

$A : 1s^2\ 2s^2$ $B : 1s^2\ 2s^2\ 2p^6\ 3s^1$

$C : 1s^2\ 2s^2\ 2p^4$ $D : 1s^2\ 2s^2\ 2p^3$

Which of these electronic configurations would you expect to have the highest?

(*i*) IE_1 (*ii*) IE_2

◑ **19.** For each of the following pairs, predict which one has lower first ionization enthalpy:

(*a*) N or O (*b*) Cl or F (*c*) Na or Na^+

(*d*) K or Ar (*e*) Kr or Xe

◑ **20.** The ionization enthalpy of hydrogen is 1312.0 kJ mol^{-1}. Express the value in eV per atom using the relation 1 eV = 1.602×10^{-19} J.

◑ **21.** Among the element Li, K, Ca, S and Kr which one is expected to have the lowest first ionization enthalpy and which the highest first ionization enthalpy?

◑ **22.** Predict which atom in each of the following pairs has the greatest first ionization enthalpy and explain your answer.

(*i*) B and C (*ii*) N and O (*iii*) Fe and Ne.

Answers to Practice Problems

18. (*i*) D (*ii*) B **19.** (*a*) O (*b*) Cl (*c*) Na (*d*) K (*e*) Xe.
20. 13.60 eV per atom **21.** Lowest : K, highest : Kr.
22. (*i*) C (*ii*) N (*iii*) Ne.

ELECTRON GAIN ENTHALPY

Just as energy is required to remove an electron from an atom, energy is released when an electron is added to a neutral atom. This is called electron gain enthalpy. Thus, **electron gain enthalpy** is

the energy released when electron is added to an isolated gaseous atom to form the gaseous negative ion.

In other words, electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form an anion as :

$$A\ (g) + e^-\ (g) \longrightarrow A^-\ (g)\quad \Delta H = \Delta_{eg} H$$

It is represented as $\Delta_{eg}H$ and is expressed in kilojoules per mole (kJ mol^{-1}). It may be noted that, in general, **electron gain enthalpy may be regarded as enthalpy change when an electron is added to an isolated gaseous atom.** This is because, the electron gain process may be **exothermic** or **endothermic**. For many elements, energy is released when an electron is added to the atom and therefore, electron gain enthalpy is **negative.** For example, elements of group 17 have very high negative electron gain enthalpy values because they have strong tendency to accept an electron to acquire stable noble gas configurations. On the other hand, noble gases have large positive electron gain enthalpies because they have no tendency to accept the electron. When they gain an electron, it enters the next higher principal quantum number leading to unstable electronic configurations.

As the definition implies, the magnitude of the electron gain enthalpy measures the ability of an atom to hold an additional electron. If an atom has more tendency to accept an electron, large energy will be released. Consequently, electron gain enthalpy will be highly negative. On the other hand, if an atom has less tendency to hold the electron, small amount of energy will be released, leading to a small negative value of electron gain enthalpy.

Factors on which Electron Gain Enthalpy depends

There are many factors which govern the electron gain enthalpy but the following are some important factors on which it mostly depends :

(*i*) **Nuclear charge.** The electron gain enthalpy become more negative as the nuclear charge increases. This is due to greater attraction for the incoming electron if nuclear charge is high.

(*ii*) **Size of the atom.** With the increase in size of the atom, the distance between the nucleus and the incoming electron increases and this results in lesser attraction. Consequently, the electron gain enthalpy become less negative with increase in size of the atom of the element.

(*iii*) **Electronic configuration.** The elements having *stable electronic configurations of half filled and completely filled valence subshells show* very small tendency to accept additional electron and thus electron gain enthalpies are less negative.

Periodic trends

Due to the lack of sufficient data, the changing trends in electron gain enthalpies on moving down a group along the period in the periodic table are less well defined than those for ionisation enthalpies. However, it has been observed (Table 18) that the electron gain enthalpy, *in general, becomes more negative from left to right in a period and becomes less*

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Table 18. Electron gain enthalpies of some elements (kJ mol^{-1}).

H							He
−73							+ 48
Li	Be	B	C	N	O	F	Ne
− 60	≈0	− 83	− 127	≈0	− 141	− 328	+ 116
Na	Mg	Al	Si	P	S	Cl	Ar
− 53	≈0	− 50	− 119	− 74	− 200	− 349	+ 97
K	Ca	Ga	Ge	As	Se	Br	Ka
− 48	−2	− 36	− 116	− 77	− 195	− 325	+ 96
Rb	Sr				Te	I	Xe
− 47	− 5				− 190	− 295	+ 77
Cs					Po	At	Rn
−46					−174	− 270	+ 68

negative as we go from top to bottom in a group. These variations are discussed below.

(a) **Variation down a group.** On moving down a group, the size and nuclear charge increases. But the effect of increase in atomic size is much more pronounced than that of nuclear charge and thus the additional electron feels less attraction by the large atom. Consequently, electron gain enthalpy becomes less negative. This is clear from decrease of electron gain enthalpy in going from chlorine to bromine and to iodine.

(b) **Variation along a period.** On moving across a period, the size of the atom decreases and nuclear charge increases. Both these factors result into greater attraction for the incoming electron, therefore, electron gain enthalpy, in general, becomes more negative in a period from left to right. However, certain irregularities are observed in the general trend. These are mainly due to the stable electronic configurations of certain atoms.

Important Trends in Electron Gain Enthalpies

There are some important features of electron gain enthalpies of elements. These are :

(*i*) Halogens have the highest negative electron gain enthalpies. The electron gain enthalpies of the halogens (group 17 elements) are highly negative. This is due to the fact that halogens have the general electronic configuration of ns^2np^5 and have only one electron less than the stable noble gas (ns^2np^6) configurations. Thus, they have very strong tendency to accept an additional electron and their electron gain enthalpies are, therefore, highly negative.

(*ii*) Electron gain enthalpy values of noble gases are positive while those of Be, Mg, N and P are almost zero. The electron gain enthalpy values of noble gases are positive. This is because they have stable electronic configuration of $ns^2\ np^6$ and thus they have absolutely no tendency to take an additional electron. This means that the incoming electron enters the next higher principal quantum level and does not feel any attraction for the nucleus. Thus, energy is required to force the electron in their atoms and therefore, their electron gain enthalpies are positive.

Similarly, the low (almost zero) electron gain enthalpy values for Be, Mg, N and P can be explained due to the extra stability of completely filled *2s*-and*3s*-orbitals in Be ($2s^2$) and Mg ($3s^2$) respectively and of half-filled *2p*-and*3p*-orbitals in N and P respectively. Therefore, the configurations show little tendency to gain any electron and hence their electron gain enthalpies are very low (almost zero).

(*iii*) Electron gain enthalpy of fluorine is unexpectedly less negative than that of chlorine. As already explained, the electron gain enthalpy, in general, becomes less negative from top to bottom in a group. However, it is observed that F-atom has unexpectedly less negative electron gain enthalpy than Cl-atom. The electron gain enthalpy values for the halogens are shown in Fig. 12. *The less negative electron gain enthalpy value of F is due to the very small size of F-atom. As a consequence of small size, there are strong inter electronic repulsions in the relatively compact 2p -subshell of fluorine and thus the incoming electron does not feel much attraction.*

Hence, the element with most negative electron gain enthalpy is chlorine.

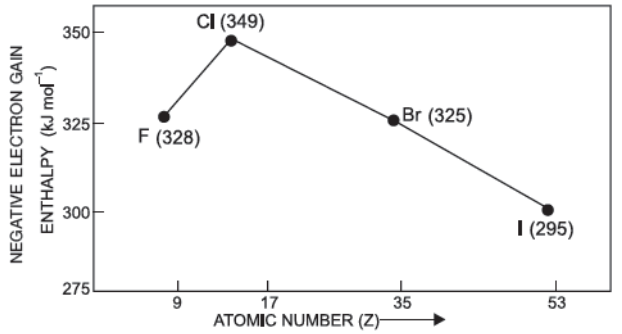

Fig. 12. Electron gain enthalpy values of the halogens.

It may be noted that, in general, the electron gain enthalpies for some third period elements (e.g. P, S, Cl) are more negative than the corresponding second period members (*e.g.* N, O, F). *This is due to the smaller size of the atoms of the second period elements which would produce larger electron-electron repulsions for the additional electron*. This effect is much more pronounced in the smallest fluorine atom as discussed above.

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Successive Electron Gain Enthalpies

Like ionization enthalpies, the second and higher electron gain enthalpies are also possible. However, the second electron is added to a negatively charged ion and the addition is opposed by coulombic repulsions. The *energy has to be supplied to force the second electron* into the anion.

First electron gain enthalpy

$O(g) + e^- \longrightarrow O^-(g)$; $\Delta_{eg}H_1 = -141$ kJ mol^{-1}

(Energy released)

Second electron gain enthalpy

$O^-(g) + e^- \longrightarrow O^{2-}(g)$ $\Delta_{eg}H_2 = +780$ kJ mol^{-1}

(Energy required to add an electron)

In other words, the second (and higher) electron gain enthalpies would have positive values. For example, the first and second electron gain enthalpy values of O, S and Se are given below.

Element	Electron gain enthalpy (kJ mol^{-1})	
	EA_1	EA_2
O	– 141	+ 780
S	– 200	+ 590
Se	– 195	+ 420

SOLVED EXAMPLES

Example 18.

Which of the following pairs of elements would have a more negative electron gain enthalpy ?

(i) O or F *(ii)* F or Cl.

Solution: *(i)* F has more negative electron gain enthalpy than O because it has $2s^2 2p^5$ configuration. It has only one electron less than the noble gas configuration. Therefore, it has strong tendency to accept an electron and its electron gain enthalpy is more negative.

(iii) Cl has more negative electron gain enthalpy than F. The less negative electron gain enthalpy of F is due to its very small size which has strong electron - electron repulsions. Therefore, F has less tendency to accept an electron and its electron gain enthalpy is less negative than Cl.

Example 19.

The electron gain enthalpy of chlorine is 349 kJmol^{-1}. How much energy in kJ is released when 1 gm of chlorine is converted completely to Cl$^-$ ions in the gaseous state? ***N.C.E.R.T.***

Solution: From the definition of electron gain enthalpy, we may write :

$Cl(g) + e^-(g) \longrightarrow Cl^-(g)$ $\Delta H = -349$ kJ mol^{-1}

Energy released when 35.5 g (1 mole) of chlorine is completely converted to $Cl^-(g)$ ions

= 349 kJ.

Energy released when 1.0 g of chlorine is completely converted to $Cl^-(g)$ ions

$$= \frac{349}{35.5} \times 1 = \mathbf{9.83\ kJ}$$

Example 20.

The amount of energy released when one million of atoms of iodine in vapour state are converted to I^- ions is 4.9×10^{-13} J according to the reaction:

$$I(g) + e^- \longrightarrow I^-(g)$$

Express the electron gain enthalpy of iodine in terms of kJ mol^{-1} and eV per atom.

Solution: The amount of energy released for the conversion of 1 million, *i.e.*, 1×10^6 atoms of iodine is 4.9×10^{-13} J according to the reaction,

$$I(g) + e^- \longrightarrow I^-(g)$$

The amount of energy released for the conversion of one mole (6.02×10^{23}) of atoms of iodine into I^- ions can be calculated. This corresponds to electron gain enthalpy. Thus,

Amount of energy released for 1×10^6 atoms of iodine $= 4.9 \times 10^{-13}$ J

Amount of energy released for 6.02×10^{23} atoms of iodine

$$= \frac{4.9 \times 10^{-13}}{1 \times 10^6} \times 6.02 \times 10^{23}$$

$= 29.5 \times 10^4$ J $= \mathbf{295\ kJ/mol}$.

Now 1 eV/atom $= 96.3$ kJ mol^{-1}

$\therefore$ Electron gain enthalpy $= -295$ kJ mol^{-1}

$$= \frac{295}{96.3} = \mathbf{-3.06\ eV/atom}$$

Example 21.

Which element will have the greatest negative electron gain enthalpy ? Give reasons.

(a) [*Ne*] $3s^2 3p^3$ *(b)* [*Ne*] $3s^2 3p^4$

(c) [*Ne*] $3s^2 3p^5$ *(d)* [*Ne*] $3s^2 3p^6 4s^1 3d^5$

Solution: The element corresponding to configuration (c) will have the highest negative electron gain enthalpy. It corresponds to chlorine (halogen) which has very strong tendency to accept an electron to acquire noble gas configuration.

Example 22.

Which of the following pairs would have a higher negative electron gain enthalpy ?

(i) N or O *(ii) F or Cl*

(iii) Br or I *(iv) B or Al*

Solution: Higher negative electron gain enthalpy :

(i) O *(ii)* Cl *(iii)* Br *(iv)* B

Example 23.

Which of the following will have the most negative electron gain enthalpy and which the least negative?

P, S, Cl, F

Explain your answer.

Solution: These elements can be arranged in different periods and groups as :

Group No.	15	16	17
2nd Period			F
3rd Period	P	S	Cl

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We know that electron gain enthalpy becomes more negaitve across a period as we move from left to right. Within the group, electron gain enthalpy becomes less negative as we move down a group. Therefore, P should have the least negative electron gain enthalpy and F should have the most negative electron gain enthalpy. However, adding an electron to smaller *2p*-orbital leads to greater inter-electronic repulsions than adding an electron to larger *3p*-orbital. Hence, Cl has more negative electron gain enthalpy than F. Therefore, Cl has the most negative electron gain enthalpy and P has the least negative electron gain enthalpy.

Practice Problems

23. Arrange the following electronic configurations in order of increasing negative electron gain enthalpy :
(*i*) $1s^2\,2s^2\,2p^6\,3s^2\,sp^5$ (*ii*) $1s^2\,2s^2\,2p^5$
(*iii*) $1s^2\,2s^2\,2p^3$ (*iv*) $1s^2\,2s^2\,2p^6\,3s^1$

24. Which of the following pairs has higher negative electron gain enthalpy?
(*i*) O, S (*ii*) F, Cl (*iii*) O, O^- (*iv*) O or F

25. Arrange the following elements in the decreasing order of negative electron gain enthalpy : B, C, N, O

26. The electron enthalpies of halogens become less negative in the order F > Cl > Br > I. Comment on the statement.

Answers to Practice Problems

23. (*iii*), (*iv*), (*ii*), (*i*)

24. (*i*) S (*ii*) Cl (*iii*) O (*iv*) F

25. O, C, B, N

26. Statement is wrong, correct order is F < Cl > Br > I

ELECTRONEGATIVITY

Electronegativity provides a qualitative measure of the ability of an atom in a chemical compound to attract shared pair of electrons towards itself. We know that a covalent bond is formed by mutual sharing of electrons between two atoms. However, all covalent bonds are not similar. In order to understand the nature of a covalent bond between atoms, a new concept known as electronegativity was introduced by Pauling. **Electronegativity** is defined as :

the tendency of an atom of an element to attract the shared pair of electrons towards itself in a covalent bond.

Greater the electronegativity of an atom, greater will be its tendency to attract the shared pair of electrons towards itself. Fluorine atom has the greatest power of attracting electrons and is the most electronegative element. It must be remembered that unlike other atomic properties such as ionisation enthalpy, electron gain enthalpy which are related to individual gaseous atoms, the electronegativity is related to atoms in the bonded state. Electronegativity values of different elements are not measured but are derived indirectly by different methods. Consequently, a number of relative scales of electronegativity such as Pauling scale, Mulliken–Jaffe scale, Allred–Rochow scale have been proposed. Among these, the most commonly used scale is that proposed by Pauling which is based upon the values of bond enthalpies of different bonds.

Pauling Scale of Electronegativity

In 1932, Linus Pauling was the first to propose a scale of electronegativity. This scale was based on the bond enthalpies in heteronuclear bonds. He suggested that if two atoms A and B had the same electronegativity values, then the bond enthalpy of A—B bond would be equal to the geometric mean of the bond enthalpies of A—A and B—B bonds. For example, the bond enthalpy of A—B molecule may be written as :

$$E_{AB} = (E_{AA} \times E_{BB})^{1/2}$$

This relation is based on the assumption of pure covalent bonds in A_2, B_2 and AB molecules. However, Pauling observed that for most of the A—B bonds, the actual bond enthalpy is more than the geometric mean of bond enthalpies of E_{AA} and E_{BB}. This means that the two participating atoms have different tendencies to attract the shared pair of electrons i.e., have different electronegativities. The difference between the actual bond enthalpy of A—B(E_{AB}) and the geometric mean bond enthalpy $[(E_{AA} \times E_{BB})^{1/2}]$ is known as **excess bond enthalpy** (ΔE). It is a measure of difference in electronegativities of two atoms A and B. By calculating ΔE for different bonds, Pauling suggested the following relationship between the electronegativities of two atoms χ_A and χ_B and the excess bond enthalpy, ΔE.

$$|\chi_A - \chi_B| = 0.12(\Delta E)^{1/2}\,\text{kJmol}^{-1}$$

It follows from the above relation that if E(A–B) is markedly different from the geometric mean of the covalent (A–A) and (B–B) bonds, then there is large electronegativity difference between the two atoms A and B. Assigning an arbitrary value of one of the element, the electronegativity values of other elements can be easily calculated. **Pauling assigned the value of 4.0 to the most electronegative element fluorine.** The Pauling electronegativity values are given in Table 20 for normal elements. These are most commonly used values.

The main **disadvantage** of Pauling scale is that the bond enthalpies are not known with good degree of accuracy for many elements. However, the values are relative values.

Mulliken scale of electronegativity

Robert Mulliken suggested another useful scale of electronegativity in terms of ionization enthalpy and electron gain enthalpy. We know that the tendency of an atom to lose an electron is related to its ionization enthalpy and the tendency of an atom to gain an electron is related to its electron gain enthalpy. This means that an atom having a high ionization enthalpy and a more negative electron gain enthalpy will attract electrons towards itself and hence will be more electronegative. On the other hand, an atom with low

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ionization enthalpy and a less negative electron gain enthalpy will have little tendency to attract electrons to itself and therefore, will have a low electronegativity.

Mulliken suggested that the tendency of an atom to attract the shared pair of electrons towards itself in a bond is the average of the ionization enthalpy ($\Delta_i H$) and electron gain enthalpy ($\Delta_{eg} H$). Therefore, Mulliken electronegativity is given as :

$$\chi_M = \frac{\Delta_i H - \Delta_{eg} H}{2}$$

where, $\Delta_i H$ = Ionization enthalpy

and $\Delta_{eg} H$ = Electron gain enthalpy.

The physical picture of Mulliken is reasonable because the tendency of an atom to attract the shared pair of electrons in a bond should be the average of the tendency of an atom to hold its own electrons ($\Delta_i H$ and its tendency to attract the additional electron $\Delta_{eg} H$).

In addition, two more electronegativity scales; Allred and Rochow scale and Sanderson's scale of electronegativity were proposed. The electronegativity values of Pauling are given in Table 19.

Factors Affecting Electronegativity

Electronegativity of an atom is not a fixed quantity but depends upon the following factors:

1. Oxidation state. In general, *the electronegativity increases as the positive oxidation state of the atom increases.* This is because with the increase in positive oxidation state, the tendency to attract the electons will increase. For example, Pauling electronegativity value for Fe(II) is 1.83 whereas it is about 1.96 for Fe(III). Some common examples are :

T1(I)	1.62	Sn(II)	1.80	Fe(II)	1.83	Cu(I)	1.90
T1(III)	2.04	Sn(IV)	1.96	Fe(III)	1.96	Cu(II)	2.00

For *anions, however, the electronegativity decreases with the increasing negative charge of the ion.* This is due to the fact that a more negatively charged ion will attract less electrons than a less negatively charged (or neutral) ion.

2. Type of hybridisation. The type of hydridisation also affects the electonegativity of an atom. We have learnt that *s*-orbitals are nearer to the nucleus than *p*, *d* and *f*-orbitals because of their higher penetration power. Therefore, *s*-orbitals will have greater electron attracting power or electronegativity. In other words, *the electronegativity increases with the increasing s-character of the hybrid orbitals* for carbon.

Hydrocarbon	Type of hybridisation	*s*-character	Electro-negativity
Methane, CH_4	sp^3	25%	2.48
Ethylene, C_2H_4	sp^2	33%	2.75
Acetylene, C_2H_2	sp	50%	3.29

The *s*-character increases in the order CH_4, C_2H_4 and C_2H_2 and the electronegativity of carbon in these compounds also increases. Similarly, for nitrogen atom, the values of the electronegativity are 3.68, 3.94 and 4.67 for sp^3, sp^2 and sp hybridisation respectively.

3. Nature of the substituents. The electronegativity of group varies with the nature of the substituents. This is due to the inductive effect of the substituent group. For example,

$CH_3 = 2.30$ $CCl_3 = 3.30$ $CF_3 = 3.35$

In these cases, the electronegativites of these groups will be the electronegativity of carbon as it is adjusted by the presence of substituents (3H, 3Cl or 3F atoms).

Periodic Variation of Electronegativity

(*a*) In a period. The electronegativity generally increases on moving across a period from left to right (*e.g.*, from Li to F). This is primarily due to decrease in atomic size and increase in effective nuclear charge. As a result of increase in effective nuclear charge, the attraction for the outer electrons and the nucleus increases in a period and therefore, electronegativity also increases.

(*b*) In a group. Electronegativity genearlly decreases from top to bottom in a group as atomic size increases and the bonding electrons become away from the nucleus. This trend is similar to that of ionization enthalpy.

It is clear from Table 19 that the electronegativity generally increases on moving across a period from left to right and decreases on moving down a group. These trends are similar to that of ionization enthalpy.

Thus, the alkali metals of group I have the lowest electronegativities and the halogens of group 17 have the highest electronegativities.

Table 19. Electronegativites of some elements (kJ mol^{-1}).

H						
2.1						
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca	Ga	Ge	As	Se	Br
0.8	1.0	1.6	1.8	2.0	2.4	2.8
Rb	Sr	In	Sn	Sb	Te	I
0.8	1.0	1.7	1.7	1.9	2.1	2.4
Cs	Ba	Tl	Pb	Bi	Po	At
0.7	0.9	1.8	1.7	2.0	1.9	2.2

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Electronegativity and metallic and non-metallic character

Non-metallic elements have strong tendency to gain electrons. Therefore, electronegativity is directly related to the non-metallic properties of elements. Alternatively, electronegativity is inversely related to metallic properties of the elements. Thus, the increase in electronegativity along a period is accompanied by increase in non-metallic properties or decrease in metallic properties. Similarly, the decrease in electronegativity down a group is accompanied by decrease in non-metallic properties or increase in metallic properties of the elements. Thus, fluorine with the highest electronegativity of 4.0 is the most non-metallic element while cesium with the lowest electronegativity of 0.7 is the most metallic element. The elements with the high electronegativities on the right-hand side of the periodic table are non-metallic elements while those having low electronegativities on the left hand side are metallic elements.

In general, as an approximation, elements with electronegativity 2.0 or greater are non–metals while those with electronegativity less than 2.0 are metals. The electronegativity helps in predicting the polar or non-polar bonds in molecules (discussed in unit 4).

Differences between electron gain enthalpy and electronegativity

The main points of difference between electron gain enthalpy and electronegativity are summed up below :

Electron gain enthalpy	Electronegativity
1. It is the tendency of an isolated gaseous atom to attract an electron.	1. It is the tendency of an atom in a molecule to attract the shared pair of electrons.
2. It is the property of isolated atoms.	2. It is the property of a bonded atom.
3. It is the absolute electron attracting power of an atom.	3. It is the relative attracting power of an atom.
4. It can be experimentally measured.	4. It cannot be measured experimentally. It is only a relative number.
5. It has units such as kJ mol^{-1} or eV/atom.	5. It has no units. There are only scales for comparison.
6. The electron gain enthalpy of an atom is constant.	6. The electronegativity of an atom is not constant. It depends upon the oxidation state of an atom, hybridisation state of the atom and the nature of substituents attached to it.

PERIODIC TRENDS IN CHEMICAL PROPERTIES

The periodic properties play central role in the study of chemistry of elements and their compounds. The periodic trends of these properties in the periodic table *i.e.*, along the periods and groups also govern to large extent the chemical behaviour. The main trends in periodic properties of elements are summed up in Fig. 13. Most of these trends in chemical properties such as *diagonal relationship, inert pair effect, effects of lanthanoid contraction etc.* will be learnt during the detailed study of the chemistry of different blocks. Some very common properties such as valence shown by elements and the *anomalous properties of the second period* (from lithium to fluorine) are taken up here.

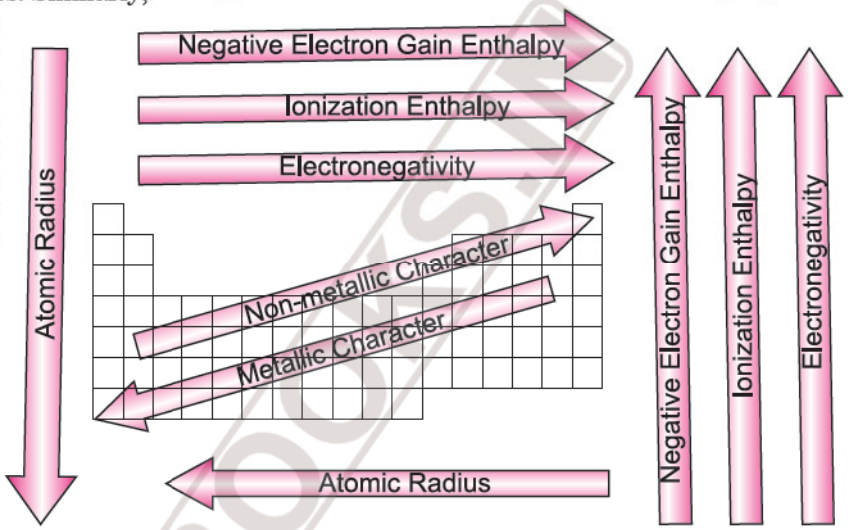

Fig. 13 Periodic trends of elements in the periodic table.

1. Periodicity of valence or oxidation states

The valence is the most characteristic property of the elements. It has been observed that the chemical properties of elements depend upon the number of electrons present in the outermost shell of the atom. ***The electrons present in the outermost shell are called valence electrons*** and *these electrons determine the valence of the atom.*

In case of representative elements, the valence is generally equal to *either number of valence electrons or equal to eight minus the number of valence electrons.* This is shown in Table 20 ahead.

However, the transition elements exhibit variable valency.

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Table 20. Valence of elements in different groups.

Group	1	2	13	14	15	16	17	18
No. of valence electrons	1	2	3	4	5	6	7	8
Valence	1	2	3	4	3, 5	2, 6	1, 7	0, 8

Variation of valency in the Periodic Table

(*a*) **Variation in a period.** The number of valency electrons increases from 1 to 8 on moving across a period, the valency of the elements with respect to hydrogen and chlorine increases from 1 to 4 and then decreases to zero. This may be illustrated by taking the examples of elements of second and third periods as given in Table 21. The number in brackets represents the valency of the elements in the compound.

Table 21. Variation of valency of elements of second and third period.

Group	1	2	13	14	15	16	17
			Elements of second period				
	Li	Be	B	C	N	O	F
Valence with respect to H							
	LiH (1)	BeH_2 (2)	BH_3 or B_2H_6 (3)	CH_4 (4)	NH_3 (3)	H_2O (2)	HF (1)
Valence with respect to Cl							
	LiCl (1)	$BeCl_2$ (2)	BCl_3 (3)	CCl_4 (4)	NCl_3 (3)	Cl_2O (2)	ClF (1)
			Elements of third period				
	Na	Mg	Al	Si	P	S	Cl
Valence with respect to H							
	NaH (1)	MgH_2 (2)	AlH_3 (3)	SiH_4 (4)	PH_3 (3)	H_2S (2)	HCl (1)

(*b*) **Variation in a group.** On moving down a group, the number of valence electrons remains same and, therefore, all the elements in a group exhibit same valency. For example, all the elements of group 1 have valency one and those of group 2 have valency two.

The periodic trends in valence of representative elements shown by the formulae of their hydrides and oxides are given in Table 22 below.

Table 22. Periodic trends in valence of elements as shown by the formulae of their compounds.

Group Period	1	2	13	14	15	16	17
Formulae of hydrides	LiH NaH KH	CaH_2 RbH	B_2H_6 AlH_3	CH_4 SiH_4 GeH_4 SnH_4	NH_3 PH_3 AsH_3 SbH_3	H_2O H_2S H_2Se H_2Te	HF HCl HBr HI
Formulae of oxides	Li_2O Na_2O K_2O Cs_2O	BeO MgO CaO Rb_2O BaO	B_2O_3 Al_2O_3 Ga_2O_3 SrO	CO_2 SiO_2 GeO_2 In_2O_3 PbO_2	N_2O_3, N_2O_5 P_4O_6, P_4O_{10} As_2O_3, As_2O_5 SnO_2 Bi_2O_3	SO_2, SO_3 SeO_2,SeO_3 Sb_2O_3, Sb_2O_5	Cl_2O_7 TeO_3

There are many elements which exhibit variable valence. This is particularly characteristic of transition elements and actinoids. These will be studied later.

Nowadays, the term **oxidation state** is preferred and frequently used for valence. **Oxidation state** of an element in a particular compound gives the *charge acquired by its atoms on the basis of electronegativity consideration from other atoms in the molecule*. Let us consider two oxygen containing compounds : OF_2 and Na_2O. The order of electronegativity of the three atoms involved in these compounds is F > O > Na. Fluorine, has the electronic configuration $2s^2 2p^5$ and each of the atom of fluorine shares one electron with oxygen in OF_2 molecule. Since fluorine is highest electronegative element, it is given oxidation state – 1. Now there are two fluorine atoms in the molecule, oxygen with outer electronic configuration $2s^2 2p^4$ share two electrons with fluorine atoms. Therefore, it shows oxidation state of +2. However, in Na_2O, oxygen being more electronegative accepts two electrons, one from each of the two sodium atoms and thus exhibits oxidation state of –2. On the other hand, sodium with electronic configuration $3s^1$ loses one electron to oxygen and therefore, exhibits oxidation state of +1. The

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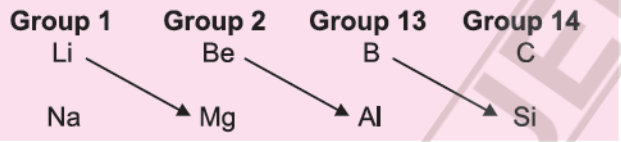
determination of oxidation state is discussed in Unit 8. The common oxidation states of representative elements are given in Table 23 ahead.

It is clear from Table 23 that *s*-block elements show only one oxidation state either +1 (alkali metals) or +2 (alkaline earth metals). Hence, *p*-block elements show different oxidation states.

2. Anomalous Properties of Second Period Elements

As we have learnt that the elements in a group show similar physical and chemical properties. However, the first element of each of the groups *i.e.*, lithium (of group 1), beryllium (of group 2) and boron to fluorine (of groups 13–17) differ in many respects from the other members of their respective groups. For example, lithium shows an anomalous behaviour as compared to sodium and rest of the family members of the alkali metal family. It forms compounds with pronounced covalent character whereas other members of the group predominantly form ionic compounds. Similarly, beryllium, the first member of alkaline earth metals family differ from other family members. It forms covalent compounds unlike other alkaline earth metals which form mainly ionic compounds. In fact, it has been observed that some elements of second period show similarities with the elements of the third period present diagonally to each other, though belonging to different groups. For example, lithium resembles with magnesium (of group 2) and beryllium resembles with aluminium (of group 3) and so on. **This similarity in properties of elements present diagonally** is called **diagonal relationship.**



For example, as shown below, metallic radii and ionic radii of Li are close to Mg but these are quite different from sodium.

Property	Element		
Metallic radius	Li	Be	B
(pm)	152	111	88
	Na	Mg	Al
	186	160	143
Ionic radius	Li^+	Be^{2+}	
(pm)	76	31	
	Na^+	Mg^{2+}	
	102	72	

The anomalous behaviour of first member of each group as compared to other group members is mainly due to the following reasons :

(*i*) Small size of the atom and its ion.
(*ii*) Large charge / radius ratio.
(*iii*) High electronegativity.
(*iv*) Non availability of *d*-orbitals in their valence shells.

The above factors have strong affects on the chemistry of first element as compared to other elements (specially second). The first member differs from its succeeding members in some of the properties as given below

(*i*) As we go down a group, the size goes on increasing, therefore, the first member of each group has the smallest size in its group.
(*ii*) Because of small size the first member has largest ionization enthalpy and ionization enthalpy decreases down the group.
(*iii*) All the elements of second period have abnormally low negative electron gain enthalpy than the second member. For example, the electron gain enthalpy decreases as we move down a group but the first member has abnormally lower electron gain enthalpy than the second because of its small size.
(*iv*) The small size of the atom results in relatively high cohesive properties associated with relatively strong intermetallic bonding. On the other hand, large atoms usually form weak bonds, therefore, the bond strengths of the compounds decrease as we move down the group. For example, lithium has relatively high enthalpy of atomization, melting and boiling points, density and hardness.
(*v*) The first member has higher electronegativity as compared to other members of the group. Therefore, it has greater tendency to form covalent bonds. For example, lithium halides, are covalent while halides, of other members of group 1 are ionic in nature.
(*vi*) The first member of the group has no vacant *d–orbitals* in its valence shell. Therefore, it has only four valence orbitals (2*s* and 2*p*) available for bonding. Therefore, the maximum covalency of the first member of each group is only 4. On the other hand, the elements of third period (second member of the group) have vacant *3d-orbitals* in their valence shell. Therefore, these have nine valence orbitals (3*s*, 3*p* and 3*d*) and therefore these elements can expand their valence shell to accommodate more than four pairs of electrons and can show valency more than 4. In other words, elements of second period cannot extend their octets while the elements of higher periods can extend their octets. For example, boron forms $[BF_4]^-$ while aluminium froms AlF_6^{3-} in solution.

Further more, the first member of *p*–block elements display greater ability to form $p\pi$ -$p\pi$ multiple bonds to itself (e.g. C = C, C ≡ C, N ≡ N) and to other elements (*e.g.*, C = O, C ≡ N, N = O, etc.). However, the other members cannot form stable $p\pi - p\pi$ multiple bonds.

Periodic Trends and Chemical Reactivity

We have learnt the periodic trends in some fundamental properties such as atomic and ionic radii, ionization enthalpy, electron gain enthalpy and, electronegativity and valence. The periodicity in these properties are related to electronic configurations. Since the chemical and physical properties of the elements and compounds are a manifestation of the electronic

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Table 23. Common oxidation states of representative elements.

I (1)	II (2)		III (13)	IV (14)	V (15)	VI (16)	VII (17)	VIII (18)
H +1 HCl -1 Na^+H^-								He
Li +1 Li^+Cl^-	Be +2 $BeCl_2$		B +3 BCl_3	C -4 CH_4 +4 CO_2 +2 CO_2	N -3 NH_3 +2 NO +3 N_2O_3 +4N_2O_4 +5 N_2O_5	O -2 H_2O -1 H_2O_2	F -1 Na^+F^-	Ne
Na +1 Na^+Cl^-	Mg +2$Mg^{2+}(Cl^-)_2$		Al +3 Al_2Cl_6	Si -4 SiH_4 +4 $SiCl_4$	P -3 PH_3 +3 PCl_3 +5 PCl_5	S -2 H_2S +4 SO_2 +6 SO_3	Cl -1 Na^+Cl^- +1 HOCl +3 $HClO_2$ +5 $HClO_3$ +7 $HClO_4$	Ar
K +1 K^+Cl^-	Ca +2 $Ca^{2+}(Cl)_2$		Ga +3 Ga_2Cl_6	Ge +4 $GeCl_4$ +2 $GeCl_2$	As -3 AsH_3 +3 $AsCl_3$ +5 As_4O_{10}	Se -2 H_2Se +4 SeO_2 +6 SeO_3	Br -1 Na^+Br^- +1 HOBr +5 $HBrO_3$ +7 $HBrO_4$	Kr +2 KrF_2
Rb +1 Rb^+Cl^-	Sr +2 $Sr^{2+}(Cl^-)_2$		In +3 $InCl_3$	Sn +4 $SnCl_4$ +2 $SnCl_2$	Sb -3 SbH_3 +3 $Sb^{3+}(F^-)_3$ +5 $SbCl_5$	Te -2 H_2Te +4 TeO_2 +6 TeO_3	I -1 Na^+I^- +1 HOI +3 HIO_3 +5 HIO_4	+2 XeF_2 +4 XeF_4 +6 XeF_6 +8 Na_4XeO_6
Cs +1 Cs^+Cl^-	Ba +2 $Ba^2(Cl^-)_2$		Tl +3 TlF_3 +1 Tl^+Cl^-	Pb +4 PbO_2 +2 $Pb^+(Cl^-)_2$	Bi -3 BiH_3 +3 $Bi(F^-)_3$ +5 Bi_2O_5	Po +4 PoO_2	At	Rn

d- B L O C K

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configuration of elements, therefore, the chemical reactivity of the elements are also governed by these fundamental properties.

The atomic and ionic radii generally decrease in a period from left to right. As a result, the ionization enthalpies in general increase (with some exceptions) and electron gain enthalpies become more negative across a period. In other words, the ionization enthalpy of the extreme left element in a period is the least and therefore, it will have highest tendency to lose electron and this tendency decreases as we move in the period from left to right. Similarly, with the exception of noble gases the electron gain enthalpy of the element on the extreme right is the highest negative showing that it has strongest tendency to gain electron and form negative ion. Noble gas element is an exception because it has filled shells and have rather positive electron gain enthalpy values. Therefore, these are least reactive. Thus, **we see that there is high chemical reactivity at two extreme ends and the lowest in the centre**.

Thus, the maximum chemical reactivity at the extreme left (among alkali metals) is exhibited by the easy loss of electrons forming a cation and at the extreme right (among halogens) shown by gain of electrons forming an anion. This property of losing or gaining electrons can be related with oxidising and reducing behaviour of the elements. The elements which readily lose electrons act as strong reducing agents while those which readily accept electrons act as strong oxidising agents. These you will learn in Unit 8. However, this tendency of an element to lose or gain electrons is also related to *metallic* or *non-metallic* character. The metals have strong tendency to lose electrons. Thus, the metallic character of an element is highest at the extreme left and decreases from left to right. On the other hand, the non-metallic character is highest at the extreme right. In other words, the metallic character decreases and non-metallic character increases from left to right across the period. For example, Li is strongest metal while F is strongest non-metal.

Second period	Li	Be	B	C, N, O, F, Ne
	Metals		Metalloid	Non-metals
Third period	Na, Mg, Al		Si	S, Cl, Ar
	Metals		Metalloid	Non-metals

Metallic character decreases →

Non-metallic character increases →

The chemical reactivity of an element can best be shown by its reactions with oxygen and halogen. Elements on the two extremes of a period readily combine with oxygen to form oxides. The normal oxide formed by the element on the extreme left (most metallic) is most basic (Na_2O) wheras, the oxide formed by the element on the extreme right (most non–metallic) is most acidic (*e.g.*, Cl_2O_7). Oxides of the elements in the centre are amphoteric (*e.g.*, Al_2O_3) or neutral (*e.g.*, CO, NO, N_2O, etc.). The amphoteric oxides show the acidic and basic character. They behave as acidic with bases and basic with acids. On the other hand, the neutral oxides have no acidic or basic properties. In general, on moving across a period from left to right, the basic character of the oxides decreases while acidic character increases. For example, on moving across the third period, it is observed that Na_2O is strongly basic, MgO is less basic, Al_2O_3 is amphoteric, SiO_2 is weakly acidic, P_2O_5 is acidic, SO_3 is strongly acidic and Cl_2O_7 is very strongly acidic.

Element	Na	Mg	Al	Si	P	S	Cl
Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Behaviour	Strongly Basic	Basic	Amphoteric	Weakly acidic	Acidic	Strongly acidic	Very strongly acidic

Acidic character increases →

As we go down the group, *the basic character of the oxides increases or acidic character decreases.* For example, in group 13, B_2O_3 is acidic, Al_2O_3 and Ga_2O_3 are amphoteric while In_2O_3 is basic.

ACIDIC CHARACTER ↓ BASIC CHARACTER ↓

Group I		Group II		Group III	
Li_2O	basic	BeO	amphoteric	B_2O_3	acidic
Na_2O	basic	MgO	basic	Al_2O_3	amphoteric
K_2O	basic	CaO	basic	Ga_2O_3	amphoteric
				In_2O_3	basic

← **BASIC CHARACTER**

ACIDIC CHARACTER →

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It may be noted that among transition elements (3*d* series), the change in atomic radii is much smaller as compared to those of representative (*s* and *p*–block) elements across the period. This changes in atomic radii is still smaller among inner transition metals (*4f*–series). The ionization enthalpies of *d*– and *f*– block elements are intermediate between those of *s*– and *p*–blocks. As a result, ***d*-and *f*-block elements are less electropositive than group 1 and group 2 metals**.

In a group, the increase in atomic and ionic radii with increase in atomic number generally results in a gradual decrease in ionization enthalpies and a regular decrease (with some exceptions) in electron gain enthalpies in case of main group elements. Thus, the metallic character increases down the group and non-metallic character decreases. For example, in 4th group, C is typical metal, Si and Ge are non-metals while Sn and Pb are typical metals. This bond can also be related with their reducing and oxidising properties which you will learn later. However, in case of transition elements, a reverse trend is observed which can be explained in terms of atomic size and ionization enthalpy.

SOLVED EXAMPLES

❑ **Example 24.**

Predict the formulae of compounds which might be formed by the following pairs of elements :

(i) Silicon and Bromine

(ii) Aluminium and Sulphur

Solution: (*i*) Silicon belongs to group 14 having a valence of 4 and bromine belongs to group 17 (halogen family) with a valence of 1. Therefore, the formula of compound formed would be **$SiBr_2$.**

(*ii*) Aluminium belongs to group 13 with a valence of 3 while sulphur belongs to group 16 with a valence of 2. Hence, the formulae of the compounds formed would be **Al_2S_3**.

❑ **Example 25.**

Are the oxidation state and covalency of Al in $[AlCl(H_2O)_5]^{2+}$ same ?

Solution: No, the oxidation state of Al is +3

covalency is 6

❑ **Example 26.**

Show by chemical reaction with water that Na_2O is a basic oxide and Cl_2O_7 is an acidic oxide.

Solution: Na_2O reacts with water and forms a strong base

$$Na_2O + H_2O \longrightarrow 2NaOH$$

Cl_2O_7 reacts with water to form a strong acid.

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$$

Their acidic and basic nature can be qualitatively tested with litmus paper. As we know acids turn blue litmus paper red while bases turn red litmus paper blue.

add on Conceptual Questions 2

CONCEPTUAL QA

Q. 1. What is the significance of the terms "isolated gaseous atom" and "ground state" while defining the ionization enthalpy and electron gain enthalpy? *N.C.E.R.T.*

Ans. Isolated gaseous atom means that the atom should be free from other atoms in the gaseous state. No energy should be required to separate it further from other atoms. Ground state means the lowest energy state possible for that atom. These terms are used for comparison purposes.

Q. 2. Energy of an electron in the ground state of the hydrogen atom is -2.18×10^{-18}J. Calculate the ionization enthalpy of atomic hydrogen in terms of J mol^{-1} ? *N.C.E.R.T.*

Ans. Ionization enthalpy is the amount of energy required to remove the electron from ground state to infinity.

Energy of electron in ground state = -2.18×10^{-18}J

Energy of electron at infinity = 0

$\therefore$ Energy required to remove electron = $0 - (-2.18) \times 10^{-18}$J = 2.18×10^{-18}J

Amount of energy required to remove 1 mol of electrons from 1 mol of H atoms

$= 2.18 \times 10^{-18} \times 6.022 \times 10^{23}$

$\therefore$ Ionization enthalpy of hydrogen = 13.130×10^5 Jmol^{-1}

= **13.13×10^5 Jmol^{-1}.**

Q. 3. The electron gain enthalpy values of halogens become more negative in the order :

F > Cl > Br > I

Comment on the statement.

Ans. This statement is wrong because the actual order is :

Cl > F > Br > I

In general, electron gain enthalpy becomes less negative down the group but F has abnormally less negative electron gain enthalpy than Cl because of its small size.

Q. 4. Calcium (Z = 20) loses electrons successively to form Ca^+, Ca^{2+} and Ca^{3+} ions. Which step will have highest ionization enthalpy?

Ans. The step which involves the formation of Ca^{3+} from Ca^{2+} : would have highest ionisation enthalpy.

$$Ca^{2+} \longrightarrow Ca^{3+} + e^-$$

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Q. 5. Which of the two : Na or Mg has higher second ionization enthalpy ?

Ans. Na.

Q. 6. Which atom or ion has the largest size ?

$Mg, Na, Na^+, Mg^{2+}, Al^{3+}, Al$?

Ans. Na.

Q. 7. Arrange the following elements in order of increasing ionization enthalpy :
B, C, N, O

Ans. B < C < O < N.

Q. 8. Consider the ground state electronic configurations given below :

(A) $1s^2\ 2s^2\ 2p^6$ **(B)** $1s^2\ 2s^2\ 2p^4$

(C) $1s^2\ 2s^2\ 2p^6\ 3s^2$ **(D)** $1s^2\ 2s^2\ 2p^6\ 3s^1$

(E) $1s^2\ 2s^2\ 2p^5$

(*i*) Which of the above configuration is associated with the lowest and which is associated with highest ionization enthalpy ?

(*ii*) Arrange the above configurations in order of increasing negative electron gain enthalpy.

Ans. (*i*) Lowest ionisation enthalpy = D
Highest ionisation enthalpy = A

(*ii*) Order of increasing negative electron gain enthalpy is :

A < C < D < B < E

Q. 9. How would you explain the fact that the first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium ?

N.C.E.R.T.

CONCEPTUAL QA

Ans. The electronic configuration of Na is [Ne] $3s^1$ and that of Mg is [Ne] $3s^2$. The configuration of Mg is more stable (being completely filled) than that of Na. Therefore, first ionization enthalpy of Mg is more than that of Na . After the loss of an electron from Na, it acquires the electronic configuration of noble gas, Ne, i.e., $1s^2 2s^2 2p^6$. On the other hand, in case of Mg atom, the electronic configuration becomes [Ne] $3s^1$. Thus, the electronic configuration of Na^+ is more stable than Mg^+ and hence the second ionization enthalpy of Na is much larger than that of Mg.

$$Na([Ne]3s^1) \xrightarrow{IE_1} Na^+([Ne]) \xrightarrow{IE_2} Na^{2+}(1s^2 2s^2 2p^5)$$

$$Mg([Ne]3s^2) \xrightarrow{IE_2} Mg^{2+}([Ne]3s^1) \xrightarrow{IE_2} Mg^{2+}([Ne])$$

$$IE_1(Na) < IE_1(Mg) \qquad IE_2(Na) > IE_2(Mg)$$

Q. 10. Among the second period elements the actual ionization enthalpies are in the order :

Li < B < Be < C < O < N < F < Ne

Explain why :

(*i*) Be has higher $\Delta_i H$ than B

(*ii*) O has lower $\Delta_i H$ than N and F

N.C.E.R.T.

Ans. (*i*) Be has higher $\Delta_i H$ than B because Be has the electronic configuration $1s^2 2s^2$ while B has the electronic configuration $1s^2 2s^2 2p^1$. The larger $\Delta_i H$ of Be in comparision to B is due to the fact that

(*a*) The electronic configuration of Be is more stable (completely filled 2*s* orbitals) than that of B.

(*b*) In Be, the electron to be removed during the ionization is an *s*-electron while the electron to be removed during ionization of B is a *p*–electron. The penetration of a 2*s*–electron to the nucleus is more than that of a 2*p*–electron and hence 2*p* electron of B is more shielded from the nucleus by the inner core of electrons than the 2*s*–electron of Be. As result, 2*s*-electron is attracted to the nucleus more than 2*p*-electron. Therefore, it is difficult to remove a 2*s*–electron from Be than to remove the 2*p*–electron from B. Thus, Be has higher ionization enthalpy than B.

(*ii*) Oxygen has four electrons in 2*p* orbitals and two of the four 2*p* electrons must occupy the same 2*p*-orbital resulting in increased electron-electron repulsion. On the other hand, N has stable half filled configuration, while F has greater nuclear charge. Therefore, O has ionization enthalpy less than N as well as F.

Q. 11. Identify the best choice in the list :

(*i*) Largest ionic size : $Mg^{2+}, Ca^{2+}, Ba^{2+}$

(*ii*) Smallest size : I^+, I^-, I

(*iii*) Highest negative electron gain enthalpy : Br, Cl, F

Ans. (*i*) Ba^{2+} (*ii*) I^+ (*iii*) Cl

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Q. 12. Arrange the following in the decreasing negative electron gain enthalpy : B, C, N, O

Ans. O, C, B, N

Q.13. Which of the following has highest ionization enthalpy : C, N and O and why ?

Ans. N has highest ionisation enthalpy because of stable exactly half filled $2p$ orbitals.

Q.14. Arrange the following in the increasing order of their size : F^-, Li^+, Na^+, Cl^-

Ans. $Li^+ < Na^+ < F^- < Cl^-$.

Q.15. A student reported the radii of Al^{3+}, Mg^{2+} and F^- as 136 pm, 65 pm and 50 pm respectively. Is the order correct ? Comment.

Ans. The order is not correct. The correct order should be Al^{3+}, Mg^{2+} and F^- as 50 pm, 65 pm and 136 pm respectively.

Q.16. Among the elements Li, K, Ca, S and Kr which one is expected to have the lowest first ionization enthalpy and which the highest first ionization enthalpy ?

Ans. Lowest ionization enthalpy : K; Highest ionization enthalpy : Kr.

Q.17. The first (IE_1) and second (IE_2) ionization enthalpies (kJ mol^{-1}) of three elements A, B and C are given below :

	A	B	C
IE_1	403	549	1142
IE_2	2640	1060	2080

Identify the element which is likely to be

(*i*) a non metal (*ii*) an alkali metal (*iii*) an alkaline earth metal *N.C.E.R.T.*

Ans. (*i*) C is non metal

(*ii*) A is alkali metal

(*iii*) B is alkaline earth metal.

Q.18. Among the elements B, Al, C and Si

(*i*) Which has the highest first ionization enthalpy ?

(*ii*) Which has the most negative electron gain enthalpy ?

(*iii*) Which has the largest atomic radius ?

(*iv*) Which has the most metallic character ?

Ans. (*i*) C (*ii*) C (*iii*) Al (*iv*) Al.

Q.19. Select from each group, the species having the smallest radius :

(*i*) K^+, Sr^{2+}, Ar (*ii*) Si, P, Cl (*iii*) O, O^-, O^{2-}

Ans. (*i*) K^+ (*ii*) Cl (*iii*) O.

Q.20. The first (IE_1) and the second (IE_2) ionization enthalpies (kJ mol^{-1}) of a few elements designated by Roman numerals are shown below :

Element	IE_1	IE_2
I	2372	5251
II	520	7300
III	900	1760
IV	1680	3380

Which of the above elements is likely to be

(*a*) a reactive metal

(*b*) a reactive non-metal

(*c*) a noble gas

(*d*) a metal that froms a stable binary halide of the formulae AX_2 (X = halogen).

Ans. (*a*) Element II (*b*) Element IV (*c*) Element I (*d*) Element III.

Q.21. Which of the elements Na, Mg, Si and P would have the greater difference between the first and the second ionization enthalpies ? Briefly explain your answer. *N.C.E.R.T.*

Ans. Among these elements, Na is an alkali metal and has only one electron in its valence shell ($3s^1$). Therefore, its IE_1 is very low. After the removal of one electron, it acquires neon gas configuration *i.e.*, ($1s^2 2s^2 2p^6$). Therefore, its IE_2 is expected to be very high. Consequently, the difference in first and second ionization enthalpies would be greatest in case of Na.

CONCEPTUAL QA

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Chapter Summary

Key Terms & Laws

- **Modern Periodic law.** The physical and chemical properties of the elements are periodic function of their atomic numbers.
- **Period.** A horizontal row in the periodic table. The elements in a period have same number of electron shells *i.e.* principal quantum number (n). There are **seven periods** in the periodic table.
- **Group.** A vertical column in the periodic table. It constitutes a series of elements whose atoms have the same outermost (or valence) electronic configuration.
- **Periodicity.** The recurrence of similar properties of the elements after certain regular intervals when they are arranged in the order of increasing atomic numbers.
- **Covalent radius** is one half of the distance between the centres of nuclei of the similar atoms bonded by a single covalent bond.
- **Van der Waals radius** is one half of the distance betwen two adjacent atoms belonging to the nearest neighbouring atoms of the substance in the solid state.
- **Ionization enthalpy.** The energy required to remove the most loosely held electron from the gaseous isolated state of an atom.
- **Electron gain enthalpy.** The energy released when an electron is added to the gaseous isolated state of an atom.
- **Electronegativity** is the tendency of an atom to attract the shared pair of electrons to itself in a bond.

QUICK CHAPTER ROUND UP

PERIODICITY

⇓

the recurrence of similar properties of the elements after certain regular intervals when arranged in the increasing order of atomic numbers is called **periodicity.**

Cause of periodicity

is the repetition of similar electronic configurations of the atoms in their valence shell after certain regular intervals.

MODERN PERIODIC LAW

- *Physical and chemical properties are periodic functions of atomic number*

LONG FORM OF PERIODIC TABLE

- 7 horizontal rows ⟶ periods
- 18 vertical columns ⟶ groups

First period	⟶ 1*s*	⟶ 2 elements
Second period	⟶ 2*s*, 2*p*	⟶ 8 elements
Third period	⟶ 3*s*, 3*p*	⟶ 8 elements
Fourth period	⟶ 4*s*, 3*d*, 4*p*	⟶ 18 elements
Fifth period	⟶ 5*s*, 4*d*, 5*p*	⟶ 18 elements
Sixth period	⟶ 6*s*, 4*f*, 5*d*, 6*p*	⟶ 32 elements
Seventh period	⟶ 7*s*, 5*f*, 6*d*, 7*p*	⟶ 32 elements

FOUR BLOCKS

***s*, *p*, *d* and *f*-Blocks**

- ***s*-block** refers to groups of elements which involve the filling of *s*-orbitals of their valence shell.
  General electronic configuration : ns^{1-2}
- ***p*-block** refers to groups of elements which involve the filling of *p*-orbitals of their valence shell.
  General electronic configuration : ns^2np^{1-6}
- ***d*-block** refers to groups of elements which involve the filling of *d*-orbitals of last but one shell.
  General electronic configuration : $(n-1)d^{1-10}ns^{0-2}$
- ***f*-block** refers to groups of elements which involve the filling of *f*-orbitals of the third to the outermost shell.
  General electronic configuration :

$$(n-2)f^{1-14}(n-1)d^{0-2}ns^2$$

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General Behaviour of Physical Properties

Atomic radius → Decreases along a period
Increases down a group
Cation < Atom
Anion > Atom

Ionisation enthalpy → Increases along a period
Decreases down a group
Li < Be > B < C < N > O < F < Ne

❑ **Isoelectronic ions** (Same number of electrons)
$N^{3-} > O^{2-} > F^{-} > Na^{+} > Mg^{2+} > Al^{3+}$

❑ Successive ionisation enthalpies are higher
$IE_3 > IE_2 > IE_1$

Negative electron gain enthalpy → Increases along a period
Decreases down a group

❑ Chlorine has highest negative electron gain enthalpy in the peridic table.

- halogens have highest negative electron gain enthalpies
- F has low negative electron gain enthalpy than Cl
- Noble gases, Be, Mg, N, P have almost zero electron gain enthalpy

Electronegativity → Increases along a period
Decreases down a group
F is the most electronegative element in the periodic table

❑ Electronegativity increases with increase *s*-character of hybrid orbitals for C.
CH_4 (sp^3) < C_2H_4 (sp^2) < C_2H_2 (sp)

Metallic character → Decreases along a period
Increases down a group

Non-metallic character → Increases along a period
Decreases down a group

NCERT FILE Solved

NCERT Textbook Exercise

Q. 1. * **What is the basic theme of organisation in the periodic table ?**

Ans. The basic theme of organisation of elements in the periodic table is to simplify and systematize the study of the numerous properties of all the elements and their compounds. This has been done by arranging the elements in such a way that similar elements are placed together while dissimilar elements are separated from one another. This has made the study simple to remember because the properties of the elements are now studied in the form of groups or families having similar properties rather than studying the elements individually.

Q. 2. * **Which important property did Mendeleev use to classify the elements in his periodic table and did he stick to that ?**

Ans. Mendeleev used atomic weight as the important property for the classification of elements. Mendeleev arranged all the known elements in the form of a table known as periodic table. He observed that some of the elements did not fit in very will with his scheme of classification if the order of atomic weight was strictly followed. He showed courage to ignore the order of atomic weights thinking that the atomic weight measurements might be incorrect. He placed the elements with similar properties together. For

*Questions are not in the new syllabus for C.B.S.E.

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example, iodine has lower atomic weight than tellurium (of Group VI) but he placed iodine in Group VII alongwith fluorine, chlorine and bromine because of the similarities in their properties. He even left some spaces or gaps for some undiscovered elements. By considering the properties of the adjacent elements, he predicted the properties of the undiscovered elements. Later on, when these elements were discovered, their properties were found to be exactly similar to those predicted by Mendeleev. For example, gallium and germanium were not discovered at that time, when Mendeleev formulated his periodic table and therefore, he left gaps for these elements. He not only predicted the existence of the elements but he estimated their properties. He tentatively named these elements as *eka-aluminium* and *eka-silicon*. When these elements were discovered, the prediction of Mendeleev proved to be remarkably correct. However, after the discovery of atomic number as more fundamental property than atomic weight by Moseley in 1913, the basis of classification was changed to atomic number.

Q. 3. What is the basic difference in approach between the Mendeleev's periodic law and the Modern periodic law ?

Ans. According to Mendeleev's periodic law, the physical and chemical properties of the elements are periodic function of their atomic weight. On the other hand, according to modern periodic law, the properties are periodic function of their atomic numbers.

Q. 4. On the basis of quantum numbers, justify that the sixth period of the periodic table should have 32 elements.

Ans. *Refer Conceptual Questions* 1, *Q. 1 (page 16)*

Q. 5. In terms of period and group where would you locate the element with Z = 114 ?

Ans. *Refer Conceptual Questions* 1, *Q.2 (page 16)*

Q. 6. Write the atomic number of the element present in the third period and seventeenth group of the periodic table.

Ans. Since it belongs to 3rd period, it will have outermost shell, $n = 3$. Its configuration will be $3s^2 3p^5$.
Therefore, its atomic number will be 17.

Q. 7. Which element do you think have been named by
(*i*) Lawrence Berkeley Laboratory
(*ii*) Seaborg's group ?

Ans. (*i*) Lawrencium (Z = 103)
(*ii*) Seaborgium (Z = 106)

Q. 8. Why do elements in the same group have similar physical and chemical properties ?

Ans. Elements in the same group have similar properties because they have similar outer electronic configurations. For detail, please refer Text.

Q. 9. What does atomic radius and ionic radius really mean to you ?

Ans. Atomic radius is one half of the distance between the nuclei of two covalently bonded atoms of the same element in a molecule. In case of metals, the atomic radius is called **metallic radius**. It corresponds to one half of the distance between two adjacent atoms in a crystal lattice.
Ionic radius means the size of the ion i.e., a cation or anion. This gives the effective distance from the nucleus of the ion upto which it has an influence in the ionic bond. The size of the cation is always smaller than that of the parent atom while the size of the anion is always larger than that of the parent atom.

Q. 10. How does atomic radius vary in a period and in a group ? How do you explain the variation ?

Ans. The atomic size decreases as we move from left to right in a period. This is because when we move along a period the nuclear charge increases and therefore, the attraction of the nucleus for the outer electrons increases and hence the atomic size decreases.
Within a group, the atomic size increases down the group. This is because of addition of a new energy shell at each succeeding element while the number of valence electrons remain the same. For detail, refer Text.

Q. 11. What do you understand by isoelectronic species ? Name a species that will be isoelectronic with each of the following atoms or ions.
(*i*) F^- (*ii*) Ar (*iii*) Mg^{2+} (*iv*) Rb^+

Ans. *Refer Solved Example 9 (Page 22).*

Q. 12. Consider the following species :
N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+}
(*a*) What is common in them?
(*b*) Arrange them in the order of increasing ionic radii.

Ans. (*a*) All these ions have same number (10) of electrons. Therefore, these are also called isoelectronic species.
(*b*) Since the number of electrons are same, the ionic size decreases with increase in nuclear charge. Therefore, the ions can be arranged in increasing order of ionic radii as

$$Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$$

Q. 13. Explain why cations are smaller and anions larger in radii than their parent atoms ?

Ans. A cation is formed by the loss of one or more electrons from the gaseous atom. With the loss of electrons from an atom, the magnitude of the nuclear charge remains same while the number of electrons decreases. As a result, the same nuclear charge now acts on lower number of electrons and therefore, the effective nuclear charge per electron increases. As a result, electrons are more strongly attracted and are pulled towards the nucleus and therefore, the size decreases.
The anion is formed by the gain of one or more electrons and therefore, the number of electrons increases while the magnitude of nuclear charge remains same. As a result, the electrons are less tightly held by the nucleus and therefore, the size increases.

Q. 14. What is the significance of the terms — 'isolated gaseous atom' and 'ground state' while defining the ionization enthalpy and electron gain enthalpy ?

Ans. *Refer Conceptual Questions* 2, *Q.1 (page 38)*

Q. 15. Energy of an electron in the ground state of the hydrogen atom is -2.18×10^{-18} J. Calculate the ionization enthalpy of atomic hydrogen in terms of J mol^{-1}.

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Ans. *Refer Conceptual Questions* 2, *Q.2 (page 38)*

Q. 16. Among the second period elements the actual ionization enthalpies are in the order Li < B < Be < C < O < N < F < Ne.
Explain why
(*i*) Be has higher $\Delta_i H$ than B.
(*ii*) O has lower $\Delta_i H$ than N and F ?.

Ans. *Refer Conceptual Questions* 2, *Q.10 (page 39)*

Q. 17. How would you explain the fact that the first ionization enthalpy of sodium is lower than that of magnesium but its second ionisation enthalpy is higher than that of magnesium ?

Ans. *Refer Conceptual Questions* 2, *Q.9 (page 39)*

Q. 18. What are the various factors due to which the ionization enthalpy of the main group elements tends to decreases down a group ?

Ans. Within the main group elements, the ionization enthalpy decreases regularly as we move down the group. This is due to the following factors :

(*i*) **Atomic size :** On moving down the group, there is a gradual increase in atomic size due to an additional main energy shell (*n*).

(*ii*) **Shielding effect.** There is increase in shielding effect on the outermost electron due to increase in the number of inner electrons.

(*iii*) **Nuclear charge.** In going from top to bottom in a group, the nuclear charge increases.

The effect of increase in atomic size and the shielding effect is much more than the effect of increase in nuclear charge. As a result, the electron becomes less tightly held to the nucleus as we move down the group. Hence there is a gradual decrease in the ionisation enthalpies in a group.

Q. 19. The first ionization enthalpy values (in kJ mol^{-1}) of group 13 elements are :

B	Al	Ga	In	Tl
801	577	579	558	589

How would you explain this deviation from the general trend ?

Ans. In general, ionization enthalpy in a group decreases with increase in atomic number. This is true from B to Al. However, Ga has unexpectedly higher ionization enthalpy than Al. This is because in case of Ga, there are ten *d*–electrons in its inner electronic configuration. The *d*–electrons are less penetrating and therefore, shield the nuclear charge less effectively than *s*– and *p*– electrons. As a result, the outer electron is held fairly strongly by the nucleus and therefore, ionization enthalpy increases slightly inspite of the increase in atomic size from Al to Ga. The similar increase is observed from In to Tl, which is due to the presence of 14*f*- electrons in the inner electronic configuration of Tl which have very poor shielding effect.

Q. 20. Which of the following pairs of elements would have a more negative electron gain enthalpy ?
(*i*) O or F **(*ii*) F or Cl**

Ans. (*i*) F (*ii*) Cl

Q. 21. Would you expect the second electron gain enthalpy of O as positive, more negative or less negative than the first ? Justify your answer.

Ans. The second electron gain enthalpy of oxygen would be positive. This is because after the addition of one electron, it becomes negatively charged. The second electron is added to negatively charged ion and the addition is opposed by coulombic repulsions. Therefore, energy has to be supplied to force the second electron into the anion and hence second electron gain enthalpy would be positive.

Q. 22. What is the basic difference between the terms electron gain enthalpy and electronegativity ?

Ans. Electron gain enthalpy refers to the tendency of an atom in its gaseous isolated state to accept an additional electron to form a negative ion. Electronegativity refers to the tendency of an atom to attract the shared pair of electrons towards it in a covalent bond. Thus, electron gain enthalpy is the property of isolated atoms whereas electronegativity is the property of atoms in molecules.

Q. 23. How would you react to the statement that electronegativity of N on Pauling scale is 3.0 in all its compounds ?

Ans. The electronegativity of nitrogen will not be 3.0 in all its compounds. It depends upon the other atoms attached to it. It also depends on the state of hybridisation and the oxidation state of the element.

Q. 24. Describe the theory associated with the radius of an atom as it
(*a*) gains an electron
(*b*) loses an electron.

Ans. (*a*) When an atom gains one electron to form an anion, its radius increases. The anions are always larger in size than the corresponding atoms. For reasons : *Refer answer to Q. 16.*

(*b*) When an atom loses an electron, it forms a cation and its radius decreases. The cations are always smaller in size than the corresponding atoms. For reason : *Refer answer to Q. 16.*

Q. 25. Would you expect the first ionization enthalpies for two isotopes of the same element to be the same or different ? Justify your answer.

Ans. Isotopes are atoms of the same element which have same atomic number but different mass number. Therefore, they have same number of electrons and nuclear charge (protons). Thus, they will have almost same first ionization enthalpies.

Q. 26. What are the major difference between metals and non-metals ?

Ans. Elements which have strong tendency to lose electrons to form cations are called **metals** whereas those which have a strong tendency to accept electrons to form anions are called **non-metals**. Thus, metals are strong reducing agents, they have low ionisation enthalpies, low negative electron gain enthalpies, low electronegativity, form basic oxides and ionic compounds.

On the other hand, non-metals are strong oxidising agents, they have high ionisation enthalpies, have high negative electron gain enthalpies, high electronegativity, form acidic oxides and covalent compounds.

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Q. 27. (*a*) Identify an element with five electrons in the outer subshell.
(*b*) Identify an element that would tend to lose two electrons.
(*c*) Identify an element that would tend to gain two electrons.
(*d*) Identify the group having metal, non-metal, liquid as well as gas at the room temperature.

Ans. (*a*) Chromium (Z = 24). It has five electrons in the outer $3d$ subshell.
(*b*) Magnesium (Z = 12) can lose two electrons readily.
(*c*) Oxygen (Z = 8) can gain two electrons.
(*d*) Halogens (group 17). It has metal (iodine), non-metals (F, Cl, Br), liquid bromine and gases.

Q. 28. The increasing order of reactivity among group 1 elements is Li < Na < K < Rb < Cs whereas that among group 17 elements is F > Cl > Br > I. Explain.

Ans. The elements of group 1 have only one electron in their outermost shells and therefore, have strong tendency to lose this electron. The tendency of these elements to lose the valence electron depends upon the ionization enthalpy. Since ionisation enthalpy decreases down the group, therefore, the reactivity of group 1 elements increases in the same order Li < Na < K < Rb < Cs.

On the other hand, the elements of group 17 have seven electrons in their respective valence shells and therefore, they have strong tendency to accept one more electron. The tendency to accept additional electrons depends upon the electrode potentials of group 17 elements. The electrode potential of group 17 elements decreases from F to I [F = + 2.86 V, Cl = + 1.36 V, Br = + 1.08 V and I = + 0.53 V) and therefore, their reactivities also decrease in the same order as F > Cl > Br > I.

Q. 29. Write the general electronic configuration of *s*, *p*, *d* and *f* block elements.

Ans. *s*-block : ns^{1-2}
p-block : ns^2np^{1-6}
d-block : $(n-1)\,d^{1-10}\,ns^{0-2}$
f-block : $(n-2)f^{1-14}\,(n-1)\,d^{0-1}\,ns^2$

Q. 30. Assign the position of the element having outer electronic configuration :
(*i*) $ns^2\,np^4$ for $n = 3$
(*ii*) $(n-1)\,d^2\,ns^2$ for $n = 4$
(*iii*) $(n-2)f^7\,(n-1)d^1ns^2$ for $n = 6$ in the periodic table.

Ans. (*i*) For $n = 3$, the element belongs to third period. The electronic configuration is $3d^2\,3d^4$. Since the last electron enters *p*-orbital, therefore, the element belongs to *p*-block.

Group no. of the element
= 10 + No. of electron in the valence shell
= 10 + 6 = 16
∴ Period = 3, Group = 16

(*ii*) For $n = 4$, the element belongs to fourth period. The electronic configuration is $3d^24s^2$. Since the *d*-subshell is incomplete, the element belongs to *d*-block.

Group no. = No. of electrons in $(n-2)$ subshell + No. of electrons in ns subshell
= 2 + 2 = 4
∴ Period = 4, Group = 4

(*iii*) For $n = 6$, the element belongs to sixth period. The electronic configuration is $4f^75d^16s^2$. Since the electron goes to *f*-orbital, therefore, its belongs to *f*-block.

All *f*-block elements belongs to group 3.
∴ Period = 6, Group = 3

Q. 31. The first (Δ_iH_1) and the second (Δ_iH_2) ionization enthalpies (in kJ) and ($\Delta_{eg}H$) electron gain enthalpy (in kJ mol^{-1}) of a few elements are given below :

Elements	ΔH_1	ΔH_2	$\Delta_{eg}H$
I	520	7200	–60
II	419	3051	–48
III	1681	3374	–328
IV	1008	1846	–295
V	2372	5251	+48
VI	738	1450	–40

Which of the above elements is likely to be
(*a*) the least reactive element.
(*b*) the most reactive metal.
(*c*) the most reactive non–metal.
(*d*) the least reactive non-metal.
(*e*) the metal which can form a stable binary halide of the formula MX_2 (X = halogen).
(*f*) the metal which can form predominantly stable covalent halide of the formula MX (X = halogen).

Ans. (*a*) V (*b*) II
(*c*) III (*d*) IV
(*e*) VI (*f*) I

Q. 32. Predict the formula of the stable binary compounds that would be formed by the following pairs of elements :
(*i*) Lithium and oxygen
(*ii*) Magnesium and nitrogen
(*iii*) Aluminium and Iodine
(*iv*) Silicon and oxygen
(*v*) Phosphorus and fluorine.
(*vi*) Element 71 and fluorine.

Ans. (*i*) Lithium belongs to group 1 with a valence of 1 while oxygen belongs to group 16 with a valence of 2. Hence, the formual of the compound is Li_2O.

(*ii*) Magnesium belongs to group 2 with a valence of 2 while nitrogen belongs to group 5 with a valence of 3. Hence, the formula of the compound is Mg_3N_2.

(*iii*) Aluminium belongs to group 13 with a valence of 3 and iodine belongs to group 17 with a valence of 1. Hence, the formula of compound is AlI_3.

(*iv*) Silicon belongs to group 14 with valence of 4 and oxygen belongs to group 16 with a valency of 2. Hence, the formula of the compound is SiO_2.

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(*v*) Phosphorus belongs to group 15 and it has valence 3 or 5, while fluorine belongs to group 17 with a valence of 1. Hence the formula of the compound may be PF_3 or PF_5.

(*vi*) Element 71 has three electrons in the valence shell ($4f^{14}\ 5d^1 6s^2$) and therefore has valence 3 and fluorine has valence 1. Hence the formula of the compound is EF_3 (E is the element).

Q. 33. In the modern periodic table, the period indicates the value of :

(*a*) atomic number (*b*) atomic mass

(*c*) principal quantum number

(*d*) azimuthal quantum number.

Ans. (*c*)

Q. 34. Which of the following statements related to the modern periodic table is incorrect ?

(*a*) The *p*-block has 6 columns, because a maximum of 6 electrons can occupy all the orbitals in a *p*-sub shell.

(*b*) The *d*-block has 8 columns, because a maximum 8 electrons can occupy all the orbitals in a *d*-subshell.

(*c*) Each block contains a number of columns equal to the number of electrons that can occupy that subshell.

(*d*) The block indicates value of azimuthal quantum number (*l*) for the last subshell that received electrons in building up the electronic configuration.

Ans. (*b*)

Q. 35. Anything that influences the valence electrons will affect the chemistry of the element. Which one of the following factors does not affect the valence shell ?

(*a*) Valence principal quantum number (*n*)

(*b*) Nuclear charge (Z)

(*c*) Nuclear mass

(*d*) Number of core electrons.

Ans. (*c*)

Q. 36. The size of isoelectronic species : F^-, Ne and Na^+ is affected by

(*a*) nuclear charge (Z)

(*b*) valence principal quantum number (*n*)

(*c*) electron-electron interaction in the outer orbitals

(*d*) none of the factors because their size is the same.

Ans. (*a*) The size of isoelectronic species depends upon the nuclear charge (Z)

Q. 37. Which one of the following statements is incorrect in relation to ionization enthalpy ?

(*a*) Ionization enthalpy increases for each successive electron.

(*b*) The greatest increase in ionization enthalpy is experienced on removal of electron from core noble gas configuration.

(*c*) End of valence electrons is marked by a big jump in ionization enthalpy.

(*d*) Removal of electron from orbitals bearing lower *n* value is easier than from orbital having higher *n* value.

Ans. (*d*)

Q. 38. Considering the elements B, Al, Mg and K, the correct order of their metallic character is :

(*a*) B > Al > Mg > K

(*b*) Al > Mg > B > K

(*c*) Mg > Al > K > B

(*d*) K > Mg > Al > B

Ans. (*d*) The metallic character decreases along a period from left to right. Therefore, metallic character of Al, Mg, K follows the order : K > Mg > Al. Within a group, metallic character increases from top to bottom so that B is less metallic than Al. So, the correct order is K > Mg > Al > B.

Q. 39. Considering the elements B, C, N, F, and Si, the correct order of their non-metallic character is:

(*a*) B > C > Si > N > F (*b*) Si > C > B > N > F

(*c*) F > N > C > B > Si

(*d*) F > N > C > Si > B

Ans. (*c*)

Q. 40. Considering the elements F, Cl, O and N, the correct order of their chemical reactivity in terms of oxidizing property is :

(*a*) F > Cl > O > N (*b*) F > O > Cl > N

(*c*) Cl > F > O > N (*d*) O > F > N > Cl

Ans. (*b*)

NCERT Exemplar Problems

Subjective Questions

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 64*

Short Answer Questions *carrying 2 or 3 marks*

Q.1. Explain why the electron gain enthalpy of fluorine is less negative than that of chlorine.

Ans. In fluorine, the new electron to be added goes to 2*p* subshell while in chlorine, the added electron goes to 3*p* subshell. Since the 2*p*-subshell is relatively small as compared to 3*p*-subshell, the added electron in small 2*p* subshell experiences strong interelectronic repulsions in comparison to that in 3*p* subshell in Cl. As a result, the incoming electron does not feel much attraction from the nucleus and therefore, the electron gain enthalpy of F is less negative than that of Cl.

Q. 2. All transition elements are *d*-block elements, but all *d*-block elements are not transition elements. Explain.

Ans. All the elements in between *s*-and *p*-block *i.e.*, between group 2 and 13 are called transition elements.

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Elements in which the last electron enters the *d*-orbitals of their respective penultimate shells are called *d*-block elements. According to this definition, Zn, Cd and Hg cannot be regarded as *d*-block elements because last electron in these elements enters the *s*-orbital of their outermost shells rather than *d*-orbital of their penultimate shells. Therefore, these elements should not be regarded as *d*-block elements. However, the properties of these elements resemble with *d*-block elements. Therefore, to make the study of periodic classification of elements more rational, these are studied alongwith *d*-block elements. Thus, on the basis of properties, all the transition elements are *d*-block elements but on the basis of electronic configuration, all *d*-block elements are not transition elements.

Q. 3. Identify the group and valency of the element having atomic number 119. Also predict the outermost electronic configuration and write the general formula of its oxide.

Ans. The present set up of the Long Form of the Periodic Table can accommodate at the maximum 118 elements. After this, according to Aufbau principle, 8*s* orbital should be filled. Therefore, the outer electronic configuration of element having atomic number 119 will be $8s^1$. Since it has one electron in the outermost *s*-orbital, its valency will be 1 and it should belong to group 1 alongwith alkali metals. The general formula of its oxide will be M_2O where M represents the element.

Q. 4. Ionisation enthalpies of elements of second period are given below :

Ionisation enthalpy/kJ mol^{-1} : 520, 899, 801, 1086, 1402, 1314, 1681, 2080.

Match the correct enthalpy with the elements and complete the graph given in Fig. 1. Also write symbols of elements with their atomic number.

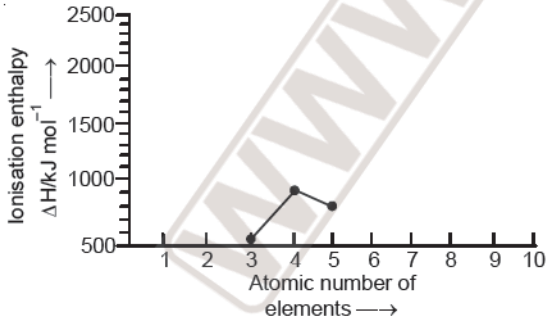

Fig. 1

Ans. *Refer Text. Page 25 and Fig.* 10.

Q. 5. Among the elements B, Al, C and Si,

(*i*) which element has the highest first ionisation enthalpy ?

(*ii*) which element has the most metallic character ?

Justify your answer in each case.

Ans. Arranging the elements into different groups and periods :

Group	13	14
Period 2	B	C
Period 3	Al	Si

(*i*) Ionization enthalpy increases along a period and decreases down a group. Therefore, C has the highest first ionization enthalpy.

(*ii*) Metallic character decreases along a period and increases down a group. Therefore, Al has the most metallic character.

Q. 6. Write four characteristic properties of *p*-block elements.

Ans. *Refer Text; Page 10.*

Q. 7. Choose the correct order of atomic radii of fluorine and neon (in pm) out of the options given below and justify your answer.

(*i*) 72, 160 (*ii*) 160, 160

(*iii*) 72, 72 (*iv*) 160, 72

Ans. Atomic radius of F is smaller than that of neon. Therefore, option (*i*) 72, 160 is correct.

Q. 8. Illustrate by taking examples of transition elements and non-transition elements that oxidation states of elements are largely based on electronic configuration.

Ans. Oxidation state depends up on the tendency to lose or gain electrons to form negatively or positively charged ions. It is the charge which an atom of the element has on its ion or appears to have when present in the combined state with other atoms. The actual sign and its magnitude depends upon the electronic configuration of the atoms. For non-transition elements, the oxidation state is equal to the number of electrons present in the outermost shell or eight minus the number of electrons present in the outermost shell. For example, *s*-block elements have either +1 (alkali metals) or +2 (alkaline earth metals) because they have 1 and 2 electrons respectively in their outermost shells and can lose these electrons. The *p*-block elements show positive, negative or even zero oxidation states. For example, elements of group 13 have three electrons in the valence shell and therefore, can show +3 oxidation state. In addition, they can also show +1 oxidation state by losing only one electron from *p*-orbitals. For example, Tl shows +1 oxidation state. Similarly, group 14 elements can exhibit +4 and +2 oxidation states and group 15 elements can exhibit a minimum oxidation state of –3 and maximum oxidation state of +5.

The transition elements (*d*-block) and inner transition elements (*f*-block) also show variable oxidation states depending upon the outermost electronic configurations. But unlike *p*-block elements, the variable oxidation states of transition and inner transition elements arise due to involvement of electrons in outermost orbitals as well as inner *d*- or *f*-electrons. For example, manganese (Z = 25) show oxidation states of +1, +2, +3, +4, +5,

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+6 and +7. All these oxidation states of non-transition elements and transition elements depend upon the electronic configurations of the atoms.

Q. 9. Nitrogen has positive electron gain enthalpy whereas oxygen has negative. However, oxygen has lower ionisation enthalpy than nitrogen. Explain.

Ans. The outermost electronic configuration of nitrogen is $2s^2 2p_x^1 2p_y^1 2p_z^1$. It is stable because it has exactly half filled $2p$-subshell. Therefore, it has no tendency to accept extra electron and energy has to be supplied to add additional electron. Thus, electron gain enthalpy of nitrogen is slightly positive. On the other hand, the outermost electronic configuration of O is $2s^2 2p_x^2 2p_y^1 2p_z^1$. It has higher positive charge (+8) than nitrogen (+7) and lower atomic size than N. Therefore, it has a tendency to accept an extra electron. Thus, electron gain enthalpy of O is negative. However, oxygen has four electrons in the $2p$ subshell and can lose one electron to acquire stable half filled configuration and therefore, it has low ionization enthalpy. Because of stable configuration of N, it cannot readily lose electron and therefore, its ionization enthalpy is higher than that of O.

Q.10. First member of each group of representative elements (*i.e.*, *s* and *p*-block elements) show anomalous behaviour. Illustrate with two examples.

Ans. *Refer Text, Page 34–36.*

Q.11. *p*-block elements form acidic, basic and amphoteric oxides. Explain each property by giving two examples and also write the reactions of these oxides with water.

Ans. The oxides of *p*-block elements show acidic, basic and amphoteric properties. The oxides formed by the elements on the extreme left (most metallic) are most basic (*e.g.*, Na_2O) whereas the oxides formed by the elements on the extreme right (most non-metallic) are most acidic (*e.g.*, Cl_2O_7). Oxides of the elements in the centre are amphoteric (*e.g.*, Al_2O_3). The amphoteric oxides show acidic as well as basic character. In general, on moving across a period from left to right, the basic character of the oxides decreases while acidic character increases. For example, or moving across the third period, the acidic and basic character of oxides is :

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Strongly basic	Basic	Amphoteric	Weakly acidic	Acidic	Strongly acidic	Very strongly acidic

Basic character decreases & Acidic character increases →

The change from basic to acidic character takes place because of increasing electronegativity of the element as we move along a period.

The oxides of elements on extreme left are basic and they react with water to form basic oxides.

$$Na_2O + H_2O \longrightarrow 2Na^+ + 2OH^-$$
$$MgO + H_2O \longrightarrow Mg^{2+} + 2OH^-$$

The oxides of elements on extreme right are acidic. For example, SO_3, P_2O_5 are acidic and these react with water as :

$$SO_3 + H_2O \longrightarrow \underset{\text{Sulphuric acid}}{H_2SO_4}$$
$$P_2O_5 + 3H_2O \xrightarrow[\text{(hot)}]{} \underset{\text{Phosphoric acid}}{2H_3PO_4}$$

The oxides of elements in centre are amphoteric. For example, B_2O_3 and Al_2O_3 are amphoteric oxides.

$$Al_2O_3 + 3H_2O \longrightarrow 2Al(OH)_3.$$

Q.12. How would you explain the fact that first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium ?

Ans. *Refer conceptual Qs.* 2 , Q. 9(*Page 39*).

Q. 13. What do you understand by exothermic reaction and endothermic reaction ? Give one example of each type.

Ans. The chemical reactions which are accompanied by evolution of heat are called **exothermic reactions.** For example,

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5 \text{ kJ}$$

The chemical reactions which proceed by the absorption of heat are called **endothermic reactions.** For example,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \; \Delta H = 92.4 \text{ kJ mol}^{-1}$$

Q. 14. Arrange the elements N, P, O and S in the order of

(*i*) increasing first ionization enthalpy.

(*ii*) increasing non-metallic character.

Give reason for the arrangement assigned.

Ans. (*i*) S < P < O < N For reasons, *refer Text, page 25.*

(*ii*) P < S < N < O For reasons, *refer Text, page 37.*

Q.15. Explain the deviation in ionization enthalpy of some elements from the general trend by using Fig. 2.

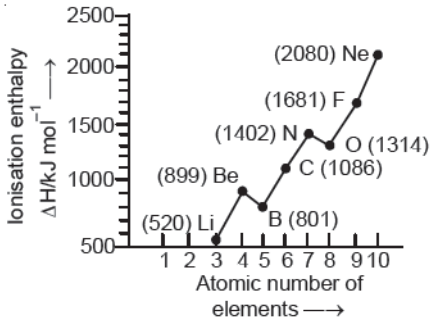

Fig. 2.

Ans. *Refer Text, page 24–25.*

Q.16. Explain the following :

(*a*) Electronegativity of elements increases on moving from left to right in the periodic table.

(*b*) Ionization enthalpy decreases in a group from top to bottom ?

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Ans. (*a*) The electronegativity generally increases on moving across a period from left to right (*e.g.*, from Li to F in the second period). This is due to decrease in atomic size and increase in effective nuclear charge. As a result of increase in effective nuclear charge, the attraction for the outer electrons and the nucleus increases in a period and therefore, electronegativity also increases.

(*b*) On moving down a group, there is a gradual decrease in ionisation enthalpy. The decrease in ionization enthalpy down a group can be explained in terms of net effect of the following factors :

(*i*) In going from top to bottom in a group, the nuclear charge increases.

(*ii*) There is a gradual increase in atomic size due to an additional main energy shell (*n*).

(*iii*) There is increase in shielding effect on the outermost electron due to increase in the number of inner electrons.

The effect of increase in atomic size and the shielding effect is much more than the effect of increase in nuclear charge. As a result, the electron becomes less and less firmly held to the nucleus as we move down the group. Hence, there is a gradual decrease in the ionisation enthalpies in a group.

Q. 17. How does the metallic and non-metallic character vary on moving from left to right in a period ?

Ans. On moving from left to right in a period, the number of electrons increases by one at each succeeding element but the number of shell remains the same. Therefore, the effective nuclear charge increases and consequently the tendency of an atom to lose electron decreases and hence metallic character decreases when we move from left to right in a period. On the other hand, with increase in nuclear charge, the tendency of an atom to gain electron increases and hence non-metallic character increases. Thus, metallic character decreases and non-metallic character increases on moving from left to right in a period.

Q. 18. The radius of Na^+ cation is less than that of Na atom. Give reason.

Ans. *Refer NCERT Text Book Exercises Q. 13.*

Q. 19. Among alkali metals which element do you expect to be least electronegative and why ?

Ans. Electronegativity decreases as the size of atom increases down a group. Therefore, francium, Fr has the least electronegativity.

Long Answer Questions *carrying 5 marks*

Q. 20. Discuss the factors affecting electron gain enthalpy and the trend in its variation in the periodic table.

Ans. *Refer Text. Page 28–29.*

Q. 21. Define ionisation enthalpy. Discuss the factors affecting ionisation enthalpy of the elements and its trends in the periodic table.

Ans. *Refer Text Page 23–25.*

Q. 22. Justify the given statement with suitable examples—"the properties of the elements are a periodic function of their atomic numbers."

Ans. *Refer Text Page 6–7.*

Q. 23. Write down the outermost electronic configuration of alkali metals. How will you justify their placement in group 1 of the periodic table ?

Ans. *Refer Text. Page 19 and Table 9.*

Q. 24. Write the drawbacks in Mendeleev's periodic table that led to its modification.

Ans. *Refer Text. Page 4.*

Q. 25. In what manner is the long form of periodic table better than Mendeleev's periodic table ? Explain with examples.

Ans. *Refer Text. Page 4,6.*

Q. 26. Discuss and compare the trend in ionisation enthalpy of the elements of group 1 with those of group 17 elements.

Ans. *Refer Text. Page 23–25.*

QUICK MEMORY TEST

A. Say True or False

1. The elements cerium (Z = 58) and neptunium (Z = 93) belong to *f*-block elements.
2. Metallic character increases from top to bottom in a group and non-metallic character increases from left to right in a period.
3. The electron gain enthalpy of oxygen is more negative than that of sulphur.
4. Among oxides of group 15, N_2O_3 is acidic while Bi_2O_3 is basic.
5. The reactivity of non-metals increases down the group from top to bottom.
6. Chlorine is the most electronegative element in the periodic table.
7. The first ionization enthalpy of Mg is higher than that of Al.
8. Cl^-, Ar and Ca^{2+} are isoelectronic species.
9. The first ionization enthalpy of O is lower than that of N.
10. The effective nuclear charge increases in a period from left to right.
11. Among O, O^- and O^{2-}, oxygen has the largest size.
12. Potassium has higher ionization enthalpy than sodium.
13. Second electron gain enthalpy of oxygen is more negative than first electron gain enthalpy.

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14. The electron gain enthalpies of noble gases are positive.
15. Among halogens, fluorine has the highest negative electron gain enthalpy.

B. Complete the missing links

1. The general electronic configuration of *d*-block elements is .....
2. Amongst the halogens, the element having highest electronegativity is .....
3. An element of group 13 which forms basic oxide is .....
4. All lanthanoids and actinoids belong to ..... block of elements.
5. The formula of compound formed with element (M) having Z = 114 and fluorine is .....
6. During the addition of second electron to oxygen, energy is .....
7. The outer electronic configuration of an element with atomic number 104 is ..... and it belongs to ..... block.
8. The IUPAC name of undiscovered element with atomic number 122 is ..... and its symbol is .....
9. The element having the configuration : $(n-1)d^2ns^2$ for $n = 4$ belongs to group ..... and period .....
10. The *p*-block has ..... columns and *d*-block has ..... columns in the periodic table.

Choose the correct alternative

1. In the series B_2O_3,CO_2 and N_2O_3, acidic character *increases/decreases*.
2. Second ionization enthalpy of Mg is *lower/higher* than that of Na.
3. Fluorine is *less/more* electronegative than chlorine.
4. The element with Z = 58 belongs to *d/f*-block.
5. The size of cation is *larger/smaller* than the parent atom.
6. Out of P^{3-}, S^{2-} and Cl^-, Cl^- has the *smallest/largest* size.
7. The second electron gain enthalpy of sulphur is *negative/positive*.
8. Ionization enthalpy *decreases/increases* down the group.
9. In the isoelectronic ions O^{2-}, F^-, Na^+, the ionic size *decreases/increases*.
10. Metallic character *increases/decreases* from left to right in a period.

Answers QUICK MEMORY TEST

A. Say True or False

1. True	2. True	3. False
4. True	5. False	6. False
7. True	8. True	9. True
10. True	11. False	12. True
13. False	14. True	15. False

B. Complete the missing links

1. $(n-1)d^{1-10}ns^{0-2}$ 2. fluorine 3. thallium
4. *f* 5. MF_4 6. supplied
7. $5f^{14}6d^27s^2$, *d* 8. unbibium, Ubb
9. 4, 4 10. 6, 10

C. Choose the correct alternative

1. increases	2. lower	3. more
4. *f*	5. smaller	6. smallest
7. positive	8. decreases	9. decreases
10. decreases.		

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. The first ionisation enthalpy of carbon atom is greater than that of boron whereas the reverse is true for the second ionisation enthalpy. Explain.

Ans. Electronic configuration of C is $1s^2\,2s^2 2p^2$ and that of B is $1s^2 2s^2 2p^1$. The nuclear charge is more in C than in B. As a result, first ionisation enthalpy of C is higher than that of B. After the removal of first electron, the second electron to be removed from C atom is from $2p$ ($2p^1$) whereas that from B atom is from $2s$ ($2s^2$). Now, $2s$ orbital is more penetrating and hence is more strongly attracted by the nucleus. As a result, second I.E. of B is higher than that of C.

Q.2. Consider the elements : N, P, O and S. Arrange them in order of

(*i*) increasing size

(*ii*) increasing first ionization enthalpy

(*iii*) increasing negative gain enthalpy

(*iv*) increasing non-metallic character.

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Ans. These elements can be arranged in different periods and groups as :

Group No.	15	16
2nd period	N	O
3rd period	P	S

(*i*) The atomic radii increase from top to bottom in a group. Therefore, N and O have smaller atomic size than that of P and S. Further, atomic size decreases along a period with increase in atomic number and therefore, the atomic size of N should be more than that of O and atomic size of P should be more than that of S. However, when we move from N to O, the nuclear charge increases by one. But at the same time, one of the *p*-orbital has two electrons which repel each other. The interelectronic repulsions in O outweigh the effect of increased nuclear charge and hence atomic size increases from N to O. However, P has less atomic size than S as expected because repulsions are not very strong in relatively larger 3*p* orbital to outweigh the effect of increased nuclear charge. Hence, the correct order of increasing atomic size is

$$N < O < S < P$$

(*ii*) Since $\Delta_i H_1$ decreases down the group, therefore, $\Delta_i H_1$ of N and O are higher than those of P and S. Further, since N has stable exactly half filled electronic configuration in the 2*p* subshell, therefore, it is difficult to remove an electron from N than from O even though O has higher nuclear charge. Similarly, P has higher $\Delta_i H_1$ than S because of stable half filled electronic configuration in the 3*p* subshell. Thus, the increasing order of first ionization enthalpy is:

$$S < P < O < N$$

(*iii*) The electron gain enthalpies of P and S are more negative than those of N and O because adding an electron to smaller size 2*p*-subshell causes greater repulsion than adding an electron to larger 3*p*-subshell. Further, N and P have stable half filled electronic configurations and therefore, have very low tendency to gain an electron. Therefore, their electron gain enthalpies are less negative. Thus, the increasing order of negative electron gain enthalpy is

$$N < P < O < S$$

(*iv*) Since non-metallic character decreases down a group and increases along a period, therefore, O is the most non-metallic element and P is the least non-metallic element. Therefore, the increasing order of non-metallic character is

$$P < S < N < O$$

Q.3. What would be the atomic number of the next
(*i*) alkali metal (*ii*) halogen and
(*iii*) noble gas
if discovered in future.

Ans. (*i*) The next alkali metal, if discovered will have to be placed in the eighth period and hence, its outermost electronic configuration will be $8s^1$. Therefore, its atomic number will be 118 + 1 = 119.

(*ii*) The next halogen, if discovered will have the outermost electronic configuration as $7s^2\ 7p^5$. The filling of 7*p* orbitals will start after filling 6*d* orbitals completely. In accordance with Aufbau principle, 6*d* orbitals will be completely filled at atomic number 112. Therefore, the atomic number of next halogen if discovered will be 112 + 5 = 117.

(*iii*) The next noble gas, if discovered will have the electronic configuration $7s^2\ 7p^6$ and hence its atomic number will be 112 + 6 = 118.

Q.4. Arrange the ions : Li^{2+}, He^+ and Be^{3+} in the increasing order of their ionic radii.

Ans. He^+, Li^{2+} and Be^{3+} are isoelectronic ions. Among isoelectronic ions, the ionic radius decreases as the positive charge increases. Hence ionic radii decreases in the order : $He^+ < Li^{2+} > Be^{3+}$.

Q.5. Which of the elements Na, Mg, Si and P would have the greater difference between the first and the second ionization enthalpies ? Briefly explain your answer.

Ans. Among these elements, Na is an alkali metal and has only one electron in its valence shell ($3s^1$). Therefore, its IE_1 is very low. After the removal of one electron, it acquire neon gas configuration i.e., ($1s^2 2s^2 2p^6$). Therefore, its IE_2 is expected to be very high. Consequently, the difference in first and second ionization enthalpies would be greatest in case of Na.

Q.6. Answer the following :
(*a*) Which has smaller size O^- or O^{2-} ?
(*b*) Which has smaller negative electron gain enthalpy F or Cl ?
(*c*) Which has lower IE_2 : Na or Mg ?
(*d*) Which has larger IE_1: N or O ?
(*e*) Which is more metallic N or K?

Ans. (*a*) O^- (*b*) F (*c*) Mg
(*d*) N (*e*) K

Q.7. Answer the following :
(*a*) Which is more basic $Mg(OH)_2$ or $Al(OH)_3$?
(*b*) Which is more acidic P_2O_5 or SiO_2 ?
(*c*) Which is less acidic H_3PO_3 or HClO
(*d*) Which is more stable Sn^{2+} or Sn^{4+} ?
(*e*) Which shows resemblances in behaviour with Al, Mg or Be ?

Ans. (*a*) $Mg(OH)_2$ (*b*) P_2O_5 (*c*) H_3PO_3
(*d*) Sn^{4+} (*e*) Be

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Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. How many groups are there in *p*-block elements and *d*-block elements ?
2. State modern periodic law.
3. How does ionisation enthalpy of the elements vary as we move across the period from left to right ?
4. Noble gases have zero electron gain enthalpy values. Explain.
5. Which is large Na^+ or K^+ ? Why ?
6. What is meant by electron gain enthalpy ?
7. Write the electronic configuration of an element with atomic number 17. To which block does this element belong ?
8. What are transition elements ? Name two transition elements.
9. From amongst Be, B and C, choose the element with the highest ionization enthalpy.
10. Give the formula of one species positively charged and one negatively charged that will be isoelectronic with Ne.
11. In terms of electronic configuration, what the elements of a given period and a group have in common ?
12. What is similar about electronic structure of Li, Na and K?
13. How many elements are present in the first transition series ?
14. Name two inner transition elements.
15. Which of the following elements are transition elements ?

    Ni, Ar, Ca, Fe, Cr, Pb
16. Predict the position of the element in the periodic table satisfying the electron configuration $(n-1)\,d^1\,ns^2$ for $n = 4$.
17. Arrange the elements B, Al, Mg and K in the increasing order of metallic character.
18. Explain why ionization enthalpies decrease down a group of the periodic table.
19. Write the IUPAC name and symbol for an element having atomic number 113.
20. Name two species which are isoelectronic with Cl^-.

Short Answer Questions *carrying 2 or 3 marks*

1. What is periodicity in elements ? What is its cause ? Explain with one example.
2. What is the basic difference in the approach between Mendeleev's periodic law and the modern periodic law?
3. Why do elements in the same group have similar physical and chemical properties ?
4. What does the atomic radius and ionic radius really mean to you ?
5. How does atomic radius vary in a period and in a group? How do you explain the variation ?
6. Explain why cations are smaller and anions larger in radii than their parent atoms ?
7. Account for the fact that the third period of the periodic table has eight and not eighteen elements.
8. Name the different blocks of elements in the periodic table. Give the general electronic configuration of each block.
9. What are transition elements ? Which of the following are not transition elements ?

    Cu(Z = 29), S(Z = 16), Ga(Z = 31), Pd(Z = 46), U(Z = 92).
10. Write the electronic configurations for the elements with atomic number 15, 21 and 37. To which blocks in the periodic table do these elements belong ?
11. Predict the periods and blocks to which each of the following elements belong ?

    (*i*) $_{13}Al$ (*ii*) $_{24}Cr$ (*iii*) $_{29}Cu$ (*iv*) $_{11}Na$.
12. What is ionization enthalpy ? How does the ionization enthalpy of the elements vary as we move down a group and along a period ?
13. Why is ionization enthalpy of B less than that of Be and of O is less than that of N?
14. Among the elements Li, Na, Mg, S and Xe, which one has the lowest first ionization enthalpy and which has the highest first enthalpy energy ?
15. Which of the following electronic configurations would you expect to have the lowest ionization enthalpy ? Explain.

    (*i*) $1s^2\,2s^2\,2p^6$

    (*ii*) $1s^2\,2s^2\,2p^5$

    (*iii*) $1s^2\,2s^2\,2p^6\,3s^1$
16. Mg^{2+} ion is smaller than O^{2-} ion although both have same electronic structure. Explain.
17. The three ionization enthalpies of boron atom are 800, 2427 and 3658 kJ mol^{-1}. Explain these values.
18. The first ionization enthalpy of C is 1086 kJ mol^{-1}. Would you expect the first ionization enthalpy of Si to be greater or lesser than this amount? Explain.
19. Describe the theory associated with the radius of atom as it

    (*a*) gains an electron

    (*b*) loses an electron
20. What are the major differences between metals and non-metals ?
21. Write the general outer electronic configurations of *s*-, *p*-, *d*- and *f*- block elements.
22. The increasing order of reactivity among group 1 elements is Li < Na < K < Rb < Cs whereas that among the group 17 elements is F > Cl > Br > I. Explain.

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23. Differentiate between ionization enthalpy and electron gain enthalpy.

24. Define atomic radius. How do the atomic radii of elements vary when we move (*i*) down a group (*ii*) across a period? How would you account for this conclusion?

25. The radii of positive ions are always smaller than the radii of the corresponding atoms. Discuss.

26. What are isoelectronic ions? Account for the decrease in size of the following isoelectronic ions :

$$O^{2-} > F^- > Na^+ > Mg^{2+}$$

27. What is screening effect? How does it govern the ionisation enthalpy of an atom?

28. Account for the difference in size of Fe^{2+} and Fe^{3+} as :

$$Fe^{2+} = 0.076 \text{ nm}$$
$$Fe^{3+} = 0.064 \text{ nm}$$

29. A, B and C are three elements. B is an inert gas other than helium. With this information complete the following table:

Element	Atomic no.	No. of electrons in the valence shell	Group to which the element belongs
A	Z – 1	.....	.....
B	Z	.....	.....
C	Z + 1	.....	.....

Also explain the following :

(*i*) Electron gain enthalpy of element is more negative than that of element C.

(*ii*) Ionization enthalpy of element C is less than that of element A

(*iii*) Electron affinity of B is zero.

30. Write the electronic configurations of the elements with atomic numbers 9, 11, 21 and 36. Stating reasons, predict the following from these configurations :

(*i*) Which of them has the lowest ionization enthalpy ?

(*ii*) Which of them has the highest negative electron gain enthalpy.

(*iii*) Which of them has positive electron gain enthalpy.

31. What do you understand by the term electron gain enthalpy? Explain why do electron gain enthalpies of the atoms become more negative. from left to right along a period in the periodic table.

32. There is a close relationship between the electronic configuration and the chemical behaviour of elements. Justify the statement giving reasons supported by two examples.

33. Account for the fact that the 4th period has eighteen and not eight elements.

34. The valency of representative elements is either equal to the number of valence electrons or eight minus this number. What is the basis of this rule?

35. Some of the periods have different number of elements than others. Explain.

36. For each of the following pairs, predict which one has greater ionisation energy and greater electron affinity :

(*a*) I, I^- (*b*) B, C (*c*) Li, Li^+.

37. Explain why electron gain enthalpy of atoms become more negative from left to right along a period in the periodic table.

38. Be in the second period of the periodic table has slightly higher first ionisation enthalpy than B.

39. Lanthanoids and actinoids are placed in separate rows at the bottom of the periodic table. Explain the reason for this arrangement.

40. The size of the cation is smaller than the size of parent atom. Explain.

41. In a period of the periodic table generally the size of an atom decreases with increase in atomic number but at the end of each period in noble gases, the atomic size increases abruptly. Explain.

42. Nitrogen has positive electron gain enthalpy whereas oxygen has negative electron gain enthalpy. However, oxygen has lower ionization enthalpy than nitrogen. Explain.

43. *p*-block elements form acidic, basic and amphoteric oxides. Explain each property by giving two examples and also write the reactions of these oxides with water.

44. Explain the following :

(*i*) Electronegativity of elements increase on moving from left to right in the periodic table.

(*ii*) Ionization enthalpy decreases in a group from top to bottom ?

45. What do you understand by the terms

(*i*) Ionization enthalpy

(*ii*) Electron gain enthalpy?

46. Explain the following :

(*i*) Ionization gain enthalpy of Mg is more than that of Na and Al.

(*ii*) Ionization gain enthalpy of nitrogen is more than that of oxygen.

(*iii*) Size of the cation is smaller than that of the neutral atom while the size of the anion is more.

47. Explain the term electron gain enthalpy. Discuss the factors which influence its value.

48. Why is ionization enthalpy of Be more than that of B? Explain.

49. How does the metallic and non-metallic character vary on moving from left to right in a period ?

50. Among alkali metals which element do you expect to be least electronegative and why ?

51. How would you explain the fact that first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium ?

52. Arrange the elements N, P, O and S in the order of :

(*i*) increasing first ionization enthalpy.

(*ii*) increasing non-metallic character.

Give reason for the arrangement assigned.

53. Why does the first ionization enthalpy increase as we go from left to right across a given period of the periodic table?

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54. Explain why ionization enthalpy decreases down the group of the Periodic Table.

55. The first ionization enthalpy of magnesium is higher than that of sodium. On the other hand, the second ionization enthalpy of sodium is very much higher than that of magnesium. Explain.

56. Which of the elements Na, Mg, Si and P would have the greatest difference between the first and the second ionization enthalpies ? Briefly explain your answer.

57. Explain the terms ionization enthalpy and electron gain enthalpy.

58. Lanthanoids and actinoids are placed in separate rows at the bottom of the Periodic Table. Explain the reason for this arrangement.

Long Answer Questions *carrying 5 marks*

1. What is modern periodic law? Discuss the main features of the long form of the periodic table. Give its important advantages and disadvantages.

2. What is ionization enthalpy ? On what factors does it depend? How does ionisation enthalpy of the elements vary as we move down a group and along a period?

3. The electronic configurations of some elements are given below :

(*i*) $1s^2, 2s^2\ 2p^6, 3s^2$ (*ii*) $1s^2, 2s^2\ 2p^6$

(*iii*) $1s^2, 2s^2\ 2p^2$ (*iv*) $1s^2, 2s^2\ 2p^6, 3s^1$

(*v*) $1s^2, 2s^2\ 2p^5$.

1. Name the elements.
2. Which of these have lowest I.E.?
3. Which is a halogen?
4. Which is an alkali metal ?
5. Which is an inert gas ?
6. Which shows a valency of 3? Justify your answers.

4. Describe the main characteristic properties of *s, p, d* and *f*-block elements.

5. Answer the following with reasons :

(*a*) Which element has higher value of negative electron gain enthalpy, F or Cl ?

(*b*) Which element has larger atomic volume, Na or K?

(*c*) Which element is more metallic, Na or Cl ?

(*d*) Which element has smaller size, O or F ?

(*e*) Which element has larger second ionization enthalpy, Na or F ?

6. Among the elements of second period (Li to Ne) pick out the element :

(*i*) with the largest atomic radius

(*ii*) with the highest ionization enthalpy

(*iii*) with the highest negative electron gain enthalpy

(*iv*) is most reactive metal

(*v*) is the most reactive non-metal.

7. The first (IE_1) and the second (IE_2) ionization energies (kJ mol^{-1}) of four elements A, B, C and D are shown below :

Elements	IE_1	IE_2
A	2372	5250
B	520	7298
C	899	1758
D	1680	3374

Which of the above elements is likely to be :

(*a*) a reactive metal

(*b*) a noble gas

(*c*) a metal that forms a stable binary halide of the formula AX_2 (X = halogen)

(*d*) a reactive non-metal.

8. Among the elements of the third period (Na to Ar), pick out the element

(*i*) with the highest ionization enthalpy

(*ii*) with the largest atomic radius

(*iii*) that is most reactive non metal

(*iv*) that is most reactive metal.

9. Discuss the following terms and account for the vacation in groups and periods of the Periodic Table :

(*i*) Electron gain enthalpy

(*ii*) Ionization enthalpy.

Hints & Answers for *Revision Exercises*

Very Short Answer Questions

1. 6, 10

5. K^+ is larger because size increases as we go down the group due to increase in principal shell.

7. *p*-block **9.** C **10.** Na^+ , F^-

11. In a period, number of shells is same.

In a group, electrons in the outermost shell are same.

13. Ten **15.** Ni, Fe, Cr

16. period 4, group 11. **17.** K, Mg, Al, B

19. Ununtrium : Uut **20.** Ar, K^+

Short Answer Questions

10. *p, d, s.*

11. (*i*) *p*-block, 3rd period (*ii*) *d*-block, 4th period (*iii*) *d*-block, 4th period (*iv*) *s*-block, 3rd period

30. (*i*) 11, (*ii*) 9, (*iii*) 36

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Long Answer Questions *carrying 5 marks*

3. 1. (*i*) Magnesium, (*ii*) Neon, (*iii*) Carbon, (*iv*) Sodium, (*v*) Fluorine
2.(*iv*) 3. (*v*) 4. (*iv*) 5. (*ii*) 6. none

5. (*a*) Cl (*b*) K (*c*) Na (*d*) F (*e*) Na

6. (*i*) Li (*ii*) Ne (*iii*) F (*iv*) Li (*v*) F

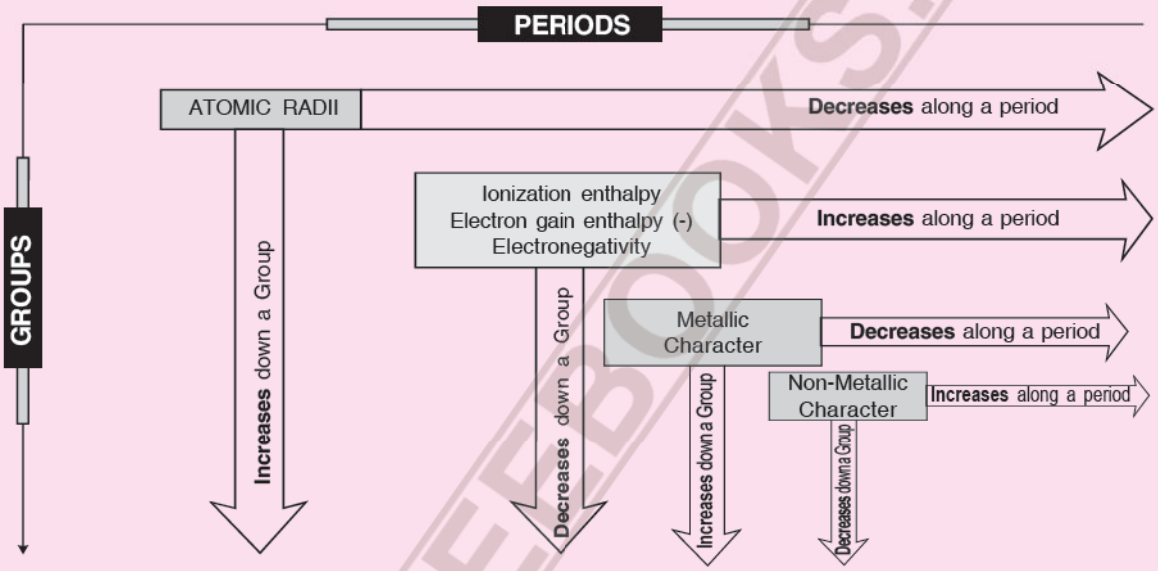
7. (*a*) B (*b*) A (*c*) C (*d*) D.

Competition File

Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

PERIODIC TRENDS



FACTS

IN THE PERIODIC TABLE

- F is most electronegative element.
- Cl has highest negative electron gain enthalpy .
- Noble gases have positive electron gain enthalpy values.
- Size decreases with increase in nuclear charge in an isoelectronic series.
- Noble gases have very high ionisation enthalpies.
- F is smallest and Li is largest in second period.
- Elements having lower ionisation enthalpies are good reducing agents.
- Elements having higher negative electron gain enthalpies are good oxidising agents.
- Elements at the two extremes of a period are most reactive.
- Fr is the largest element in the periodic table.

OBJECTIVE TYPE QUESTIONS

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Periodic Table

A1. Long form of the periodic table is based on the properties of elements as a function of :
(*a*) atomic size
(*b*) atomic mass
(*c*) electronegativity
(*d*) atomic number.

Answers

A1. (*d*)

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A2. The maximum number of elements in 3rd period is :
(a) 8 (b) 18
(c) 32 (d) between 8 and 18

A3. Which pair of atomic number represents *s*-block elements ?
(a) 7,15 (b) 6, 12
(c) 9, 17 (d) 3, 12

A4. Transition metals have the general electronic configuration :
(a) ns^2nd^{1-10} (b) $ns^2np^1(n-1)d^{1-10}$
(c) $ns^{1,2}(n-1)d^{1-10}$ (d) $ns^2np^6(n-1)d^{1-10}$

A5. The tendency towards complex formation is maximum in
(a) *s*-block elements (b) *p*-block elements
(c) *d*-block elements (d) none of these

A6. A element with atomic number 112 has recently been named as copernicium. It is named in honour of scientist astronomer Nicolaus Copernicus. Which of the following statement about this element is not correct?
(a) It belongs to *d*-block
(b) It belongs to 12th group
(c) Its electronic configuration is [Rn] $5f^{14}6d^{10}7s^2$
(d) It belongs to 6th period

A7. The recently discovered element, Meitnerium (Z = 109) belongs to :
(a) *s*-block (b) *p*-block
(c) *d*-block (d) *f*-block

A8. The fourth period of the *p*-Block elements contains :
(a) 6 elements (b) 8 elements
(c) 10 elements (d) 18 elements

A9. Elements A, B, C, D and E have the following electronic configurations :
A : $1s^22s^22p^1$ B : $1s^22s^22p^63s^23p^1$
C : $1s^22s^22p^63s^23p^3$ D : $1s^22s^22p^63s^23p^5$
E : $1s^22s^22p^63s^23p^64s^2$
The elements belonging to same group in the periodic table are:
(a) A and D (b) C and D
(c) A and B (d) A and D

A10. An element 'X' belongs to the third period of the *p*-block elements. It has four electrons in the outermost shell. The name of the element is
(a) Aluminium (b) Silicon
(c) Germanium (d) Sulphur

Periodic Properties

A11. Which of the following properties generally decreases along a period ?
(a) Atomic size
(b) Negative electron gain enthalpy
(c) Ionisation enthalpy
(d) Atomic volume

A12. The correct order or radii of three species Ca, Ca^+ and Ca^{2+} is :
(a) $Ca > Ca^+ > Ca^{2+}$ (b) $Ca^{2+} > Ca^+ > Ca$
(c) $Ca^+ > Ca > Ca^{2+}$ (d) $Ca^+ > Ca^{2+} > Ca$

A13. In the P^{3-}, S^{2-} and Cl^- ions, the increasing order of size is :
(a) Cl^-, S^{2-}, P^{3-} (b) P^{3-}, S^{2-}, Cl^-
(c) S^{2-}, Cl^-, P^{3-} (d) S^{2-}, P^{3-}, Cl^-

A14. The property which regularly increases down the group in the periodic table is :
(a) Ionisation enthalpy (b) Electronegativity
(c) Reducing nature (d) Electron gain enthalpy

A15. The ionisation gain enthalpy of nitrogen is more than that of oxygen because of :
(a) greater attraction of nucleus for the electrons
(b) the extra stability of half filled *p*-orbitals
(c) smaller size of the nitrogen atom
(d) more penetrating effect.

A16. The correct order of increasing radii of the elements Na, Si, Al and P is :
(a) Si, Al, P, Na (b) Al, Si, P, Na
(c) P, Si, Al, Na (d) Al, P, Si, Na

A17. Which of the following electronic configurations corresponds to elements with largest negative electron gain enthalpy ?
(a) $1s^2\,2s^2\,2p^5$ (b) $1s^2\,2s^2\,2p^6$
(c) $1s^2\,2s^2\,2p^6\,3s^2\,3p^5$ (d) $1s^2\,2s^2\,2p^6\,3s^1$

A18. In which of the following pairs, the first atom or ion is not larger than the second ?
(a) K, K^+ (b) S, O
(c) Br, Br^- (d) N, O

A19. The family of elements with the highest ionisation enthalpy :
(a) alkaline earth metals
(b) halogens
(c) noble gases
(d) alkali metals

A20. Which of the following has largest negative electron gain enthalpy ?
(a) F (b) Cl
(c) Br (d) I

A21. The anion O^- is isoelectronic with
(a) N^{2-} (b) F^-
(c) N^{3-} (d) Ne

Answers

A2. (a) **A3.** (d) **A4.** (c) **A5.** (c) **A6.** (d) **A7.** (c) **A8.** (a) **A9.** (c) **A10.** (b) **A11.** (a)
A12. (a) **A13.** (a) **A14.** (c) **A15.** (b) **A16.** (c) **A17.** (c) **A18.** (c) **A19.** (c) **A20.** (b) **A21.** (a)

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A22. The ionic size of Na^+, Mg^{2+}, Al^{3+} and Si^{4+} follows the order :
(a) $Na^+ < Mg^{2+} < Al^{3+} < Si^{4+}$
(b) $Na^+ > Mg^{2+} > Al^{3+} > Si^{4+}$
(c) $Na^+ > Mg^{2+} < Al^{3+} < Si^{4+}$
(d) $Na^+ < Mg^{2+} > Al^{3+} > Si^{4+}$

A23. Amongst the following elements (where electronic configurations are given below), the one having the highest ionisation enthalpy is :
(a) [Ne] $3s^2 3p^1$ (b) [Ne] $3s^2 3p^3$
(c) [Ne] $3s^2 3p^2$ (b) [Ne] $3d^{10} 4s^2 4p^2$

A24. The penetration of the electrons in any principal shell varies as :
(a) $s > p > d > f$ (b) $s < p < d < f$
(c) $s > p < d > f$ (d) $s < p > d > f$

A25. Which of the following oxide is most acidic ?
(a) BeO (b) MgO
(c) CaO (d) BaO

A26. Which one of the following processes proceeds with the absorption of energy ?
(a) $F(g) + e^- \longrightarrow F^-(g)$
(b) $O^-(g) + e^- \longrightarrow O^{2-}(g)$
(c) $O(g) + e^- \longrightarrow O^-(g)$
(d) $Cl(g) + e^- \longrightarrow Cl^-(g)$

A27. Which of the following statement is correct ?
(a) 1st and 2nd IE of nitrogen is more than 1st and 2nd IE of oxygen.
(b) IE of oxygen is greater than IE of nitrogen.
(c) IE_2 of oxygen is greater than IE_2 of nitrogen.
(d) all statements are correct.

A28. Ionization enthalpy of lithium is 520 kJ mol^{-1}. How much enthalpy in joules must be needed to convert all atoms of Li to Li^+ ions present in 7 mg of Li vapours.
(a) 74.3 kJ (b) $520 \times 6.023 \times 10^{-17}$ J
(c) 520 J (d) 780 J

A29. In the second period of the periodic table, ionisation enthalpy follows the order :
(a) Ne > F > O > N > C > B > Se > Li
(b) Ne > F > N > C > O > Be > B > Li
(c) Li > B > Be > C > O > N > F > Ne
(d) Ne > F > N > O > C > Be > B > Li

A30. Which of the following configuration is expected to have maximum difference in second and third ionisation enthalpies ?
(a) $1s^2 2s^2 2p^2$ (b) $1s^2 2s^2 2p^6 3s^1$
(c) $1s^2 2s^2 2p^6 3s^2$ (d) $1s^2 2s^2 2p^1$

A31. The process requiring absorption of energy is
(a) $F \rightarrow F^-$ (b) $O^- \rightarrow O^{2-}$
(c) $Cl \rightarrow Cl^-$ (d) $H \rightarrow H^-$

A32. The incorrect statements among the following is
(a) The first ionisation enthalpy of Al is less than the first ionisation enthalpy of Mg.
(b) The second ionisation enthalpy of Mg is greater than the second ionisation enthalpy of Na.
(c) The first ionisation enthalpy of Na is less than the first ionisation enthalpy of Mg.
(d) The third ionisation enthalpy of Mg is greater than the third ionisation enthalpy of Al.

A33. The amount of energy released when one million atoms of iodine in vapour state are converted to I^- ions is 4.9×10^{-13} J. The electron gain enthalpy of iodine is
(a) 4.9×10^{20} kJ mol^{-1} (b) 29.5×10^{10} kJ mol^{-1}
(c) 2.95 kJ mol^{-1} (d) 295 kJ mol^{-1}

A34. The element with highest electron gain enthalpy belongs to
(a) period 2 group 17 (b) period 3 group 7
(c) period 3 group 17 (d) period 3 group 16

A35. The five successive ionisation enthalpies of an element are 801, 2427, 3638, 25024, and 32824 kJ mol^{-1} respectively. The number of valence electrons of the atom of the element is
(a) 5 (b) 2
(c) 3 (d) 4

Answers

A22. (b) **A23.** (c) **A24.** (a) **A25.** (a) **A26.** (b) **A27.** (c) **A28.** (c) **A29.** (d) **A30.** (a) **A31.** (b)
A32. (b) **A33.** (d) **A34.** (c) **A35.** (c)

B MULTIPLE CHOICE QUESTIONS *from competitive examinations*

AIPMT & Other State Boards' Medical Entrance

B1. The electronic configuration of the atom having maximum difference in the first and the second ionization enthalpies is
(a) $1s^2 2s^2 2p^6 3s^1$ (b) $1s^2 2s^2 2p^6 3s^2$
(c) $1s^2 2s^2 2p^1$ (d) $1s^2 2s^2 2p^6 3s^2 3p^1$
(e) $1s^2 2s^2 2p^3$ *(Kerala P.M.T. 2007)*

B2. The electronic configuration of four elements are given below. Arrange these in the correct order of the magnitude (without sign) of their electron gain enthalpy
(i) $2s^2 2p^5$ (ii) $3s^2 3p^5$ (iii) $2s^2 2p^4$ (iv) $3s^2 3p^4$
Select the correct answer using the codes given below :
(a) (i) < (ii) < (iv) < (iii)
(b) (ii) < (i) < (iv) < (iii)
(c) (i) < (iii) < (iv) < (ii)
(d) (iii) < (iv) < (i) < (ii) *(Kerala P.M.T. 2007)*

B3. With which of the following electronic configuration an atom has the lowest ionization ethalpy ?
(a) $1s^2 2s^2 2p^6$ (b) $1s^2 2s^2 2p^5$
(c) $1s^2 2s^2 2p^3$ (d) $1s^2 2s^2 2p^5 3s^1$
(C.B.S.E. Med. 2007)

Answers

B1. (a) **B2.** (d) **B3.** (d)

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B4. Identify the correct order of size of the following :
(a) $Ca^{2+} < K^+ < Ar < Cl^- < S^{2-}$
(b) $Ar < Ca^{2+} < K^+ < Cl^- < S^{2-}$
(c) $Ca^{2+} < Ar < K^+ < Cl^- < S^{2-}$
(d) $Ca^{2+} < K^+ < Ar < S^{2-} < Cl^-$ *(C.B.S.E. Med. 2007)*

B5. The element with atomic number 117 has not been discovered yet. In which family would you place this element if discovered ?
(a) Alkali metals (b) Alkaline earth metals
(c) Halogens (d) Noble gases
(e) Coinage metals *(Kerala Med. 2009)*

B6. The correct order of the decreasing ionic radii in the following isoelectronic species is :
(a) $S^{2-} > Cl^- > K^+ > Ca^{2+}$ (b) $K^+ > Ca^{2+} > Cl^- > S^{2-}$
(c) $Ca^{2+} > K^+ > S^{2-} > Cl^-$ (d) $Cl^- > S^{2-} > Ca^{2+} < K^+$
(CBSE Med. 2010)

B7. Which of the following represents the correct order of increasing electron gain enthalpy with negative sign for the elements O, S, F and Cl?
(a) F < S < O < Cl (b) S < O < Cl < F
(c) Cl < F < O < S (d) O < S < F < Cl
(CBSE Med. 2010)

B8. Identify the wrong statement in the following :
(a) Amongst isoelectronic species, smaller the positive charge on the cation, smaller is the ionic radius.
(b) Amongst isoelectronic species, greater the negative charge on the anion, larger is the ionic radius.
(c) Atomic radius of the elements increases as one moves down the first group of the periodic table.
(d) Atomic radius of the elements decreases as one moves across from left to right in the 2nd period of the periodic table. *(A.I.P.M.T. 2012)*

B9. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I having atomic number 9, 17, 35 and 53 respectively, is
(a) F > Cl > Br > I (b) Cl > F > Br > I
(c) Br > Cl > I > F (d) I > Br > Cl > F
(A.M.U. Med. 2013)

B10. Which of the following pairs contain metalloid elements in the periodic table?
(a) Na and K (b) F and Cl
(c) Ca and Mg (d) As and Si
(e) Cu and Ag *(Kerala PMT 2014)*

B11. Which of the following orders of ionic radii is correctly represented?
(a) $H^- > H^+ > H$ (b) $Na^+ > F^- > O^{2-}$
(c) $O^{2-} > F^- > Na^+$ (d) $Al^{3+} > Mg^{2+} > N^{3-}$
(AIPMT 2014, Karnataka CET 2018)

B12. Among Mg, Mg^{2+}, Al and Al^{3+} which will have the largest and the smallest size respectively?
(a) Mg, Al^{3+} (b) Al^{3+}, Mg
(c) Mg^{2+}, Al (d) Al, Mg^{2+}
(e) Mg^{2+}, Al^{3+} *(Kerala PMT 2015)*

B13. The formation of the oxide ion, O^{2-} (g), from oxygen atom requires first an exothermic and then an endothermic step as shown below :
$O(g) + e^- \rightarrow O^-(g)$; $\Delta_f H^\ominus = -141$ kJ mol^{-1}
$O^-(g) + e^- \rightarrow O^{2-}(g)$; $\Delta_f H^\ominus = +780$ kJ mol^{-1}
Thus process of formation of O^{2-} in gas phase is unfavourable even though O^{2-} is isoelectronic with neon. It is due to the fact that,
(a) oxygen is more electronegative
(b) addition of electron in oxygen results in larger size of the ion.
(c) electron repulsion outweighs the stability gained by achieving noble gas configuration.
(d) O^- ion has comparatively smaller size than oxygen atom *(A.I.P.M.T. 2015)*

B14. The species Ar, K^+ and Ca^{2+} contain the same number of electrons. In which order do their radii increase?
(a) $Ca^{2+} < K^+ < Ar$ (b) $K^+ < Ar < Ca^{2+}$
(c) $Ar < K^+ < Ca^{2+}$ (d) $Ca^{2+} < Ar < K^+$
(A.I.P.M.T. 2015)

B15. In which of the following options the order of arrangement does not agree with the variation of property indicated against it?
(a) I < Br < Cl < F (increasing electron gain enthalpy)
(b) Li < Na < K < Rb (increasing metallic radius)
(c) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ (increasing ionic size)
(d) B < C < N < O (increasing first ionization enthalpy)
(NEET 2016)

B16. The element Z = 114 has been discovered recently. It will belong to which of the following family/group and electronic configuration?
(a) Carbon family, [Rn] $5f^{14}\ 6d^{10}\ 7s^2\ 7p^2$
(b) Oxygen family, [Rn] $5f^{14}\ 6d^{10}\ 7s^2\ 7p^4$
(c) Nitrogen family, [Rn] $5f^{14}\ 6d^{10}\ 7s^2\ 7p^6$
(d) Halogen family, [Rn] $5f^{14}\ 6d^{10}\ 7s^2\ 7p^5$
(NEET 2017)

B17. Magnesium reacts with an element (X) to form an ionic compound. If the ground state electronic configuration of (X) is $1s^2\ 2s^2\ 2p^3$, the simplest formula for this compound is
(a) Mg_2X_3 (b) MgX_2
(c) Mg_2X (d) Mg_3X_2 *(NEET 2018)*

JEE (Main) & Other State Boards' Engineering Entrance

B18. In which of the following arrangements, the order is not correct according to the property indicated against it ?
(a) $Al^{3+} < Mg^{2+} < Na^+ < F^-$
increasing ionic size.

Answers

B4. (a) **B5.** (c) **B6.** (a) **B7.** (d) **B8.** (a) **B9.** (b) **B10.** (d) **B11.** (c) **B12.** (a) **B13.** (c)
B14. (a) **B15.** (a, d) **B16.** (a) **B17.** (d) **B18.** (b)

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(*b*) B < C < N < O
increasing first ionization enthalpy.

(*c*) I < Br < F < Cl
increasing electron gain enthalpy (with negative sign).

(*d*) Li < Na < K < Rb
increasing metallic radius. *(A.I.E.E.E. 2005)*

B19. The increasing order of the first ionisation enthalpies of elements of B, P, S and F (lowest first) is

(*a*) P < S < B < F (*b*) B < P < S < F
(*c*) B < S < P < F (*d*) F < S < P < B
(A.I.E.E.E. 2006)

B20. In which one of the following pairs, the radius of the second species is greater than that of the first ?

(*a*) Na, Mg (*b*) O^{2-}, N^{3-}
(*c*) Li^+, Be^{2+} (*d*) Ba^{2+}, Sr^{2+}
(*e*) Al, Be *(Kerala C.E.T. 2007)*

B21.

Column I	Column II
(*a*) He	(*i*) High negative electron gain enthalpy
(*b*) Cl	(*ii*) Most electropositive element
(*c*) Ca	(*iii*) Strongest reducing agent
(*d*) Li	(*iv*) Highest ionization enthalpy

The correct match of the contents in column I with those in column II is

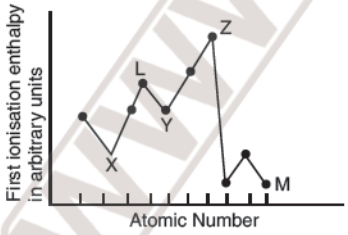
(*a*) *a–iii, b–i, c–ii, d–iv* (*b*) *a–iv, b–iii, c–ii, d–i*
(*c*) *a–ii, b–iv, c–i, d–iii* (*d*) *a–i, b–ii, c–iii, d–iv*
(*e*) *a–iv, b–i, c–ii, d–iii* *(Kerala P.E.T. 2008)*

B22. The electronic configuration of an element with maximum negative electron gain enthalpy is

(*a*) $1s^2 2s^2 2p^3$ (*b*) $1s^2 2s^2 2p^5$
(*c*) $1s^2 2s^2 2p^6 3s^2 3p^5$ (*d*) $1s^2 2s^2 2p^6 3s^2 3p^3$
(*e*) $1s^2 2s^2 2p^6 3s^1$ *(Kerala P.E.T. 2008)*

B23. In the graph below, the one which represents an alkali metal with the higher atomic number is

(*a*) X
(*b*) Y
(*c*) Z
(*d*) L
(*e*) M



(Kerala P.E.T. 2008)

B24. The correct order of ionisation enthalpy of C, N, O, F is

(*a*) C < O < N < F (*b*) C < N < O < F
(*c*) F < N < C < O (*d*) F < O < N < C
(Karnataka C.E.T. 2009)

B25. The set representing the correct order of ionic radius is

(*a*) $Li^+ > Be^{2+} > Na^+ > Mg^{2+}$
(*b*) $Na^+ > Li^+ > Mg^{2+} > Be^{2+}$
(*c*) $Li^+ > Na^+ > Mg^{2+} > Be^{2+}$
(*d*) $Mg^{2+} > Be^{2+} > Li^+ > Na^+$ *(A.I.E.E.E. 2009)*

B26. Which of the following order regarding ionization enthalpy is correct?

(*a*) N > O > F (*b*) N < O < F
(*c*) N > O < F (*d*) N < O > F
(West Bengal JEE 2010)

B27. Which of the following set will have highest hydration enthalpy and highest ionic radius?

(*a*) Na and Li (*b*) Li and Rb
(*c*) K and Na (*d*) Cs and Na
(AMU Engg. 2010)

B28. Generally, the first ionization enthalpy increases along a period. But there are some exceptions. One which is NOT an exception is

(*a*) N and O (*b*) Na and Mg
(*c*) Mg and Al (*d*) Be and B
(Karnataka CET 2010)

B29. The first ($\Delta_i H_1$) and second ($\Delta_i H_2$) ionization enthalpies (in kJ mol^{-1}) and the electron gain enthalpy ($\Delta_{eg} H$) (in kJ mol^{-1}) of the elements I, II, III, IV and V are given below:

Element	$\Delta_i H_1$	$\Delta_i H_2$	$\Delta_{eg} H$
I	520	7300	– 60
II	419	3051	– 48
III	1681	3374	– 328
IV	1008	1846	– 295
V	2372	5251	+ 48

The most reactive metal and the least reactive non-metal of these are respectively

(*a*) I and V (*b*) V and II
(*c*) II and V (*d*) IV and V
(*e*) V and III *(Kerala PET 2010)*

B30. The correct sequence which shows decreasing order of the ionic radii of the elements is :

(*a*) $Na^+ > F^- > Mg^{2+} > O^{2-} > Al^{3+}$
(*b*) $O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$
(*c*) $Al^{3+} > Mg^{2+} > Na^+ > F^- > O^{2-}$
(*d*) $Na^+ > Mg^{2+} > Al^{3+} > O^{2-} > F^-$ *(A.I.E.E.E. 2010)*

B31. The second ionization enthalpies of Li, Be, B and C are in the order

(*a*) Li > C > B > Be (*b*) Li > B > C > Be
(*c*) B > C > Be > Li (*d*) Be > C > B > Li
(J&K CET 2011)

Answers

B19. (*c*) **B20.** (*b*) **B21.** (*e*) **B22.** (*c*) **B23.** (*e*) **B24.** (*a*) **B25.** (*b*) **B26.** (*c*) **B27.** (*b*) **B28.** (*b*)
B29. (*c*) **B30.** (*b*) **B31.** (*b*)

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B32. Which of the following is the largest in size ?
(a) Cl^- (b) S^{2-}
(c) Na^+ (d) F^- *(J&K CET 2011)*

B33. Which of the following is the largest in size ?
(a) S^{2-} (b) Se^{2-}
(c) O^{2-} (d) Te^{2-} *(Odisha JEE 2011)*

B34. An element belongs to group 15 and third period of the periodic table. Its electronic configuration will be
(a) $1s^2 2s^2 2p^3$ (b) $1s^2 2s^2 2p^4$
(c) $1s^2 2s^2 2p^6 3s^2 3p^3$ (d) $1s^2 2s^2 2p^6 3s^2 3p^2$
(WB – JEE 2011)

B35. Which one of the following has the lowest ionisation enthalpy ?
(a) $1s^2 2s^2 2p^6$ (b) $1s^2 2s^2 2p^6 3s^1$
(c) $1s^2 2s^2 2p^5$ (d) $1s^2 2s^2 2p^3$ *(WB – JEE 2011)*

B36. The correct decreasing order of first ionisation enthalpies of five elements of the second period is
(a) Be > B > C > N > F (b) N > F > C > B > Be
(c) F > N > C > Be > B (d) N > F > B > C > Be
(e) F > C > N > B > Be *(Kerala PET 2011)*

B37. The correct order of decreasing electronegativity values among the elements I-beryllium, II-oxygen, III-nitrogen and IV-magnesium is
(a) II > III > I > IV (b) III > IV > II > I
(c) I > II > III > IV (d) I > II > IV > III
(e) II > III > IV > I *(Kerala PET 2011)*

B38. Generally, the first ionization energy increases along a period. But there are some exceptions. The one which is NOT and exception is
(a) Na and Mg (b) Be and B
(c) N and O (d) Mg and Al
(Karnataka CET 2011)

B39. Considering the elements B, C, N, F and Si the correct order of their non-metallic character is
(a) B > C > Si > N > F
(b) Si > C > B > N > F
(c) F > N > C > B > Si
(d) F > N > C > Si > B *(A.M.U. Engg. 2011)*

B40. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I, having atomic number 9, 17, 35 and 53 respectively, is
(a) F > Cl > Br > I (b) Cl > F > Br > I
(c) Br > Cl > I > F (d) I > Br > Cl > F
(A.I.E.E.E. 2011)

B41. Among the following, the element of highest first ionisation enthalpy is
(a) C (b) F
(c) Be (d) N
(e) Ne *(Kerala P.E.T. 2012)*

B42. The correct order of ionisation energy of C, N, O and F is
(a) F < N < C < O (b) C < N < O < F
(c) C < O < N < F (d) F < O < N < C
(Karnataka C.E.T. 2012)

B43. The correct order of electronegativities of N, O, F and P is
(a) F > N > P > O (b) F > O > P > N
(c) F > O > N > P (d) N > O > F > P
(Karnataka C.E.T. 2012)

B44. The polarizing power of the following anions N^{3-}, O^{2-} and F^-, follow the order
(a) $N^{3-} > F^- > O^{2-}$ (b) $O^{2-} > N^{3-} > F^-$
(c) $O^{2-} > F^- > N^{3-}$ (d) $N^{3-} > O^{2-} > F^-$
(A.M.U. Engg. 2012)

B45. The correct order of negative electron gain enthalpy ($\Delta_{eg}H$) of the halogen atoms is
(a) F > Cl > Br > I (b) Cl > F > Br > I
(c) I > Br > Cl > F (d) Cl > Br > I > F
(J.K.C.E.T. 2012)

B46. The increasing order of the ionic radii of the given isoelectronic species is
(a) $S^{2-}, Cl^-, Ca^{2+}, K^+$ (b) $Ca^{2+}, K^+, Cl^-, S^{2-}$
(c) $K^+, S^{2-}, Ca^{2+}, Cl^-$ (d) $Cl^-, Ca^{2+}, K^+, S^{2-}$
(A.I.E.E.E. 2012)

B47. Which one of the following sets of ions represents the collection of isoelectronic species?
(a) $K^+, Cl^-, Mg^{2+}, Sc^{3+}$
(b) $Na^+, Ca^{2+}, Sc^{3+}, F^-$
(c) $K^+, Ca^{2+}, Sc^{3+}, Cl^-$
(d) $Na^+, Mg^{2+}, Al^{3+}, Cl^-$ *(Karnataka C.E.T. 2013)*

B48. Which of the following noble gases has the highest positive electron gain enthalpy value ?
(a) Helium (b) Krypton
(c) Argon (d) Neon
(e) Xenon *(Kerala P.E.T. 2013)*

B49. Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar ?
(a) Ca < Ba < S < Se < Ar
(b) Ca < S < Ba < Se < Ar
(c) S < Se < Ca < Ba < Ar
(d) Ba < Ca < Se < S < Ar *(JEE Mains 2013)*

B50. The first ionization potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be
(a) + 2.55 eV (b) – 2.55 eV
(c) – 5.1 eV (d) – 10.2 eV
(JEE P.E.T. 2013)

B51. What are lanthanides and actinides?
(a) Inner transition elements
(b) Noble gases
(c) Normal elements
(d) Transition elements *(J.K. C.E.T. 2014)*

Answers

B32.	(b)	**B33.**	(d)	**B34.**	(c)	**B35.**	(b)	**B36.**	(c)	**B37.**	(a)	**B38.**	(a)	**B39.**	(d)	**B40.**	(b)	**B41.**	(e)
B42.	(c)	**B43.**	(c)	**B44.**	(d)	**B45.**	(b)	**B46.**	(b)	**B47.**	(c)	**B48.**	(d)	**B49.**	(d)	**B50.**	(c)	**B51.**	(a)

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B52. For one of the element, various successive ionization enthalpies (in kJ mol^{-1}) are given below:

	1st	2nd	3rd	4th	5th
I.E.	577.5	1810	2750	11,580	14,820

The element is
(a) P (b) Mg
(c) Si (d) Al
(Karnataka CET 2015)

B53. Amongst Be, B, Mg and Al, the second ionization potential is maximum for
(a) B (b) Be
(c) Mg (d) Al *(WB JEE 2015)*

B54. The ionic radii (in Å) of N^{3-}, O^{2-} and F^- are respectively
(a) 1.71, 1.40 and 1.36 (b) 1.71, 1.36 and 1.40
(c) 1.36, 1.40 and 1.71 (d) 1.36, 1.71 and 1.40
(JEE Main 2015)

B55. An element X belongs to fourth period and fifteenth group of the periodic table. Which of the following statement is true?
(a) It has a completely filled *s*-orbital and a partially filled *d*-orbital.
(b) It has completely filled *s*-and *p*-orbitals and a partially filled *d*-orbital.
(c) It has completely filled *s*-and *p*-orbitals and a half-filled *d*-orbitals.
(d) It has a half-filled *p*-orbital and completely filled *s*-and *d*-orbitals. *(WB JEE 2016)*

B56. Which of the following atom has the highest first ionization enthalpy?
(a) Rb (b) Na
(c) K (d) Sc *(JEE Main 2016)*

B57. Which of the following atom should have the highest negative first electron gain enthalpy?
(a) F (b) O
(c) N (d) C *(WB JEE 2017)*

B58. The electronegativities of C, N, Si and P are in the order of
(a) Si < P < C < N (b) Si < P < N < C
(c) P < Si < N < C (d) P < Si < C < N
(Karnataka CET 2017)

B59. The group having isoelectronic species is :
(a) $O^{2-}, F^-, Na^+, Mg^{2+}$ (b) O^-, F^-, Na, Mg^+
(c) O^{2-}, F^-, Na, Mg^{2+} (d) O^-, F^-, Na^+, Mg^{2+}
(JEE Main 2017)

B60. Which electronic configuration will show the highest first ionization enthalpy ?
(a) $1s^2 2s^2 2p^1$ (b) $1s^2 2s^2 2p^5$
(c) $1s^2 2s^2 2p^3$ (d) $1s^2 2s^2$
(J.K. C.E.T. 2018)

B61. What is the correct increasing order of ionic or atomic radii in the following ?
(a) $Si^{4+} < P^{5+} < S^{6+} < Cl^{7+}$
(b) $P^{5+} < Si^{4+} < Cl^{7+} < S^{6+}$
(c) $Cl^{7+} < S^{6+} < P^{5+} < Si^{4+}$
(d) $S^{6+} < P^{5+} < Cl^{7+} < Si^{4+}$ *(J.K. C.E.T. 2018)*

B62. Which element has the highest first ionization potential ?
(a) N (b) Ne
(c) He (d) H
(e) Li *(Kerala P.E.T. 2018)*

B63. Which statement(s) is (are) false for the periodic classification of elements ?
(a) The properties of the elements are the periodic function of their atomic numbers.
(b) Non-metallic elements are lesser in number than the metallic elements.
(c) The first ionization energies of the elements along a period do not vary in a regular manner with increase in atomic number.
(d) For transition elements, the *d*-electrons are filled monotonically with increase in atomic number.
(e) Both (c) and (d). *(Kerala PET 2018)*

B64. The electronegativities of N, C, Si and P are in the order
(a) P < Si < C < N (b) Si < P < N < C
(c) Si < P < C < N (d) P < Si < N < C
(e) difficult to predict. *(Kerala PET 2018)*

B65. The element with Z = 120 (not yet discovered) will be an/a
(a) Inner-transition metal
(b) Transition metal
(c) Alkaline earth metal
(d) Alkali metal *(JEE Main 2019)*

Answers

B52. (d) **B53.** (b) **B54.** (a) **B55.** (d) **B56.** (d) **B57.** (a) **B58.** (a) **B59.** (a) **B60.** (b) **B61.** (c)
B62. (c) **B63.** (d) **B64.** (c) **B65.** (c)

C MULTIPLE CHOICE QUESTIONS
with more than one correct answers

C1. Which of the following sets contain only isoelectronic ions ?
(a) $P^{3-}, S^{2-}, Cl^-, K^+$ (b) Na^+, K^+, Cl^-, F^-
(c) $Ti^{4+}, Sc^{3+}, Cl^-, Ar$ (d) O^{2-}, Na^{2+}, F^-, Ar

C2. Which of the following statements are not correct ?
(a) Germanium was earlier called eka-silicon
(b) Moseley introduced the concept of atomic number as the basis of modern periodic law.
(c) 14 elements of 5th period are called lanthanoids
(d) 4th period begins with rubidium.

Answers

C1. (a, c) **C2.** (c, d)

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C3. Which of the following order is not correct for first ionisation enthalpy ?
(*a*) C < N (*b*) O < S (*c*) N < O (*d*) Cl < F

C4. Which of the following trend is not correct for size ?
(*a*) Na < K < Rb (*b*) $I^+ < I^- < I$
(*c*) $Fe^{2+} < Fe^{3+} < Fe$ (*d*) F < O < N

C5. In which of the following arrangements, the order is / are not according to the property indicated :

(*a*) C < N < O	Ionization enthalpy
(*b*) $F^- < Na^+ < Mg^{2+}$	Increasing ionic size
(*c*) Br < F < Cl	Increasing negative electron gain enthalpy
(*d*) Na < K < Rb	Increasing atomic radius

C6. Which of the following donot belong to *d*-block elements?
(*a*) [Xe] $5d^1 6s^2$ (*b*) [Xe] $4f^1 5d^1 6s^2$
(*c*) [Rn] $5f^1 6d^1 7s^2$ (*d*) [Ar] $3d^{10} 4s^1$

C7. Which of the following property increases along a period (in general)
(*a*) Atomic size
(*b*) Ionisation enthalpy
(*c*) Electron gain enthalpy (negative)
(*d*) Ionic size

C8. Which of the following are correct order of ionisation enthalpy ?
(*a*) F < Cl < Br (*b*) C < O < N
(*c*) B < Al < Ga (*d*) O < S < Se

Answers

C3. (*b, c*) **C4.** (*b, c*) **C5.** (*a,b*) **C6.** (*b, c*) **C7.** (*b, c*) **C8.** (*b, d*)

D MULTIPLE CHOICE QUESTIONS
based on the given passage/comprehension

Passage - I

The properties of the elements such as atomic or ionic radii, ionisation ethalpy, electron gain enthalpy and electronegativity are directly or indirectly related to their electronic configuration and are called periodic properties. A part of the periodic table is given below :

C	N	O	F
	P	S	Cl
		Se	Br
			I

Answer the following questions :

D1. Which of the following has highest ionisation enthalpy?
(*a*) N (*b*) P (*c*) O (*d*) C

D2. Bromine belongs to period
(*a*) third (*b*) fourth (*c*) fifth (*d*) second

D3. The highest negative electron gain enthalpy is of
(*a*) F (*b*) N (*c*) S (*d*) Br

D4. Which of the following has the largest size ?
(*a*) N (*b*) O (*c*) S (*d*) P

D5. The highest ionisation enthalpy is of
(*a*) P (*b*) O (*c*) N (*d*) S

D6. Which of the following is not correct ?
(*a*) Electron gain enthalpy : Cl > F > Br
(*b*) Atomic size : N > O < F
(*c*) Ionization enthalpy : N > O > F
(*d*) Ionic size : $N^{3-} > O^{2-} > F^-$

Passage-II

In the modern periodic table, elements are arranged in order of increasing atomic numbers which is related to the electronic configuration. Depending upon the type of orbitals receiving the last electron, the elements in the periodic table have been divided into four blocks, *viz*, *s*, *p*, *d* and *f*. The modern periodic table consists of 7 periods and 18 groups. Each period begins with the filling of a new energy shell. In accordance with the Aufbau principle, the seven periods (1 to 7) have 2, 8, 8, 18, 18, 32 and 32 elements respectively. The seventh period is still incomplete. To avoid the periodic table being too long, the two series of *f*-block elements, called lanthanoids and actinoids are placed at the bottom of the main body of the periodic table.

Answer the following questions :

D7. The last element of the *p*-block in 6^{th} period is represented by the outermost electronic configuration.
(*a*) $5f^{14}\ 6d^{10}\ 7s^2\ 7p^0$ (*b*) $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$
(*c*) $4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$ (*d*) $7s^2\ 7p^6$

D8. The element with atomic number 57 belongs to
(*a*) *f*-block (*b*) *d*-block
(*c*) *p*-block (*d*) *s*-block

D9. The elements with atomic numbers 35, 53 and 85 are all
(*a*) halogens (*b*) heavy metals
(*c*) light metals (*d*) noble gases

Answers

Passage - I **D1.** (*a*) **D2.** (*b*) **D3.** (*a*) **D4.** (*d*) **D5.** (*c*) **D6.** (*b*)
Passage-II **D7.** (*c*) **D8.** (*b*) **D9.** (*a*)

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D10. The electronic configuration of the element which is just above the element with atomic number 43 in the same group is

(*a*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$

(*b*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

(*c*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2\ 4p^6$

(*d*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$

D11. Which of the elements whose atomic numbers are given below, cannot be accommodated in the present set up of the long form of the periodic table?

(*a*) 118 (*b*) 107 (*c*) 102 (*d*) 126

Answers

Passage-II **D10.** (*d*) **D11.** (*d*)

Assertion Reason Type Questions

The questions given below consists of an Assertion and the Reason. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

(*b*) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.

(*c*) If assertion is CORRECT but reason is INCORRECT.

(*d*) If assertion is INCORRECT but reason is CORRECT.

(*e*) If both assertion and reason are INCORRECT.

1. Assertion : The first ionization enthalpy of aluminium is lower than that of magnesium.
Reason : Atomic radius of aluminium is smaller than that of magnesium.

2. Assertion : Both N_2 and NO^+ are diamagnetic substances.
Reason : NO^+ is isoelectronic with N_2.

3. Assertion : F atom has less negative electron gain enthalpy than Cl atom.
Reason : Additional electrons are repelled more effectively by 3*p*–electrons in Cl than by 2*p*–electrons in F atom.

4. Assertion : The first ionization energy of Be is greater than that of B.
Reason : 2*p*-orbital is higher in energy than 2*s*-orbital.

5. Assertion : The elements having $1s^2\ 2s^2\ 2p^6\ 3s^2$ and $1s^2\ 2s^2$ configuration belong to same group.
Reason : These have same number of valence electrons.

6. Assertion : The ionic radii follow the order $I^- < I < I^+$.
Reason : These are isoelectronic species.

7. Assertion : The size decreases in the order : $O^{2-} > Mg^{2+} > Al^{3+}$.
Reason : In isoelectronic ions, the size decreases with increases in atomic number.

8. Assertion : Atomic radius in general decreases along a period.
Reason : In a period, effective nuclear charge decreases.

9. Assertion: Electron gain enthalpy becomes less negative as we go down a group.
Reason : Size of the atom increases on going down the group and the added electron would be farther from the nucleus.

10. Assertion: Boron has a smaller first ionisation enthalpy than beryllium.
Reason : The penetration of a 2*s* electron to the nucleus is more than the 2*p* electron hence 2*p* electron is more shielded by the inner core of electrons than the 2*s* electrons.

Answers

1. (*b*) **2.** (*a*) **3.** (*c*) **4.** (*a*) **5.** (*a*) **6.** (*e*) **7.** (*a*) **8.** (*c*) **9.** (*d*) **10.** (*a*).

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.

	p	q	r	s
A	(p)	(q)	(r)	(s)
B	(p)	(q)	(r)	(s)
C	(p)	(q)	(r)	(s)
D	(p)	(q)	(r)	(s)

If the correct matches are A-*q*, A-*r*, B-*p*, B-*s*, C-*r*, C-*s* and D-*q*, then the correctly bubbled matrix will look like the following:

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1. Match the elements/ions in Column I with the characteristics in Column II from left to right.

Column I	Column II
(A) Cl, Br, I	(*p*) ionisation enthalpy increases
(B) B, C, N	(*q*) negative electron gain enthalpy decreases
(C) O, O^-, O^{2-}	(*r*) atomic size decreases
(D) Cl, F, P	(*s*) belong to same period

2. Match the property given in Column I with the preoperty given in Column II

Column I	Column II
(A) Ionisation enthalpy	(*p*) decreases down the group
(B) Negative electron gain enthalpy	(*q*) increases down the group
(C) Metallic character	(*r*) increases from left to right in a period (in general)
(D) Atomic size	(*s*) decreases from left to right in a period (in general)

3. Electronic configuration of some elements is given in Column I and their first ionization enthalpies are given in Column II. Match the electronic configuration with first ionization enthalpy.

Column (I)	Column (II)
Electronic configuration	**First ionization enthalpy/kJ mol^{-1}**
(A) $1s^2\ 2s^2\ 2p^6$	(*p*) 495
(B) $1s^2\ 2s^2\ 2p^6\ 3s^1$	(*q*) 1681
(C) $1s^2\ 2s^2\ 2p^5$	(*r*) 1314
(D) $1s^2\ 2s^2\ 2p^4$	(*s*) 2080

Answers

(1): (A) – (*q*) (B) – (*p*), (*r*), (*s*) (C) – (*q*) (D) – (*q*) **(2)** : (A) – (*p*), (*r*) (B) – (*p*), (*r*) (C) – (*q*), (*s*) (D) – (*q*), (*s*)
(3): (A) – (*s*) (B) – (*p*) (C) – (*q*) (D) – (*r*)

NCERT Exemplar Problems

Objective Questions

▶ Multiple Choice Questions (Type-I) ◀

1. Consider the isoelectronic species, Na^+, Mg^{2+}, F^- and O^{2-}. The correct order of increasing length of their radii is
(*a*) $F^- < O^{2-} < Mg^{2+} < Na^+$
(*b*) $Mg^{2+} < Na^+ < F^- < O^{2-}$
(*c*) $O^{2-} < F^- < Na^+ < Mg^{2+}$
(*d*) $O^{2-} < F^- < Mg^{2+} < Na^+$

2. Which of the following is not an actinoid ?
(*a*) Curium (Z = 96) (*b*) Californium (Z = 98)
(*c*) Uranium (Z = 92)(*d*) Terbium (Z = 65)

3. The order of screening effect of electrons of *s*, *p*, *d* and *f* orbitals of a given shell of an atom on its outer shell electrons is :
(*a*) $s > p > d > f$ (*b*) $f > d > p > s$
(*c*) $p < d < s > f$ (*d*) $f > p > s > d$

4. The first ionisation enthalpies of Na, Mg, Al and Si are in the order :
(*a*) Na < Mg > Al < Si
(*b*) Na > Mg > Al > Si
(*c*) Na < Mg < Al < Si
(*d*) Na > Mg > Al < Si

5. The electronic configuration of gadolinium (Atomic number 64) is
(*a*) [Xe] $4f^8\ 5d^5\ 6s^2$ (*b*) [Xe] $4f^7\ 5d^2\ 6s^1$
(*c*) [Xe] $4f^7\ 5d^1\ 6s^2$ (*d*) [Xe] $4f^8\ 5d^6\ 6s^2$

6. The statement that is not correct for periodic classification of elements is :
(*a*) The properties of elements are periodic function of their atomic numbers.
(*b*) Non metallic elements are less in number than metallic elements.
(*c*) For transition elements, the 3*d*-orbitals are filled with electrons after 3*p*-orbitals and before 4*s*-orbitals.
(*d*) The first ionisation enthalpies of elements generally increase with increase in atomic number as we go along a period.

Answers

1. (*b*) **2.** (*d*) **3.** (*a*) **4.** (*a*) **5.** (*b*) **6.** (*c*)

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7. Among halogens, the correct order of amount of energy released in electron gain (electron gain enthalpy) is :

(*a*) F > Cl > Br > I (*b*) F < Cl < Br < I

(*c*) F < Cl > Br > I (*d*) F < Cl < Br > I

8. The period number in the long form of the periodic table is equal to

(*a*) magnetic quantum number of any element of the period.

(*b*) atomic number of any element of the period.

(*c*) maximum principal quantum number of any element of the period.

(*d*) maximum azimuthal quantum number of any element of the perod.

9. The elements in which electrons are progressively filled in 4*f*-orbital are called

(*a*) actinoids (*b*) transition elements

(*c*) lanthanoids (*d*) halogens

10. Which of the following is the correct order of size of the given species :

(*a*) $I > I^- > I^+$ (*b*) $I^+ > I^- > I$

(*c*) $I > I^+ > I^-$ (*d*) $I^- > I > I^+$

11. The formation of the oxide ion, O^{2-} (*g*), from oxygen atom requires first an exothermic and then an endothermic step as shown below :

$O(g) + e^- \longrightarrow O^-(g)$; $\Delta H^\circ = -141$ kJ mol^{-1}

$O^-(g) + e^- \longrightarrow O^{2-}(g)$; $\Delta H^\circ = +780$ kJ mol^{-1}

Thus process of formation of O^{2-} in gas phase is unfavourable even though O^{2-} is isoelectronic with neon. It is due to the fact that,

(*a*) oxygen is more electronegative.

(*b*) addition of electron in oxygen results in larger size of the ion.

(*c*) electron repulsion outweighs the stability gained by achieving noble gas configuration.

(*d*) O^- ion has comparatively smaller size than oxygen atom.

12. *Comprehension given below is followed by some multiple choice questions. Each question has one correct option. Choose the correct option.*

In the modern periodic table, elements are arranged in order of increasing atomic numbers which is related to the electronic configuration. Depending upon the type of orbitals receiving the last electron, the elements in the periodic table have been divided into four blocks, viz, *s*, *p*, *d* and *f*. The modern periodic table consists of 7 periods and 18 groups. Each period begins with the filling of a new energy shell. In accordance with the Aufbau principle, the seven periods (1 to 7) have 2, 8, 8, 18, 18, 32 and 32 elements respectively. The seventh period is still incomplete. To avoid the periodic table being too long, the two series of *f*-block elements, called lanthanoids and actinoids are placed at the bottom of the main body of the periodic table.

(*i*) The element with atomic number 57 belongs to

(*a*) *s*-block (*b*) *p*-block

(*c*) *d*-block (*d*) *f*-block

(*ii*) The last element of the *p*-block in 6th period is represented by the outermost electronic configuration.

(*a*) $7s^2\,7p^6$ (*b*) $5f^{14}\,6d^{10}\,7s^2\,7p^0$

(*c*) $4f^{14}\,5d^{10}\,6s^2\,6p^6$ (*d*) $4f^{14}\,5d^{10}\,6s^2\,6p^4$

(*iii*) Which of the elements whose atomic numbers are given below, cannot be accommodated in the present set up of the long form of the periodic table ?

(*a*) 107 (*b*) 118

(*c*) 126 (*d*) 102

(*iv*) The electronic configuration of the element which is just above the element with atomic number 43 in the same group is _____.

(*a*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,3s^2$

(*b*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^3\,4p^6$

(*c*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6\,4s^2$

(*b*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^7\,4s^2$

(*v*) The elements with atomic numbers 35, 53 and 85 are all _____.

(*a*) noble gases (*b*) halogens

(*c*) heavy metals (*d*) light metals

13. Electronic configurations of four elements A, B, C and D are given below :

(A) $1s^2\,2s^2\,2p^6$ (B) $1s^2\,2s^2\,2p^4$

(C) $1s^2\,2s^2\,2p^6\,3s^1$ (D) $1s^2\,2s^2\,2p^5$

Which of the following is the correct order of increasing tendency to gain electron :

(*a*) A < C < B < D (*b*) A < B < C < D

(*c*) D < B < C < A (*d*) D < A < B < C

Answers

7. (*c*) **8.** (*c*) **9.** (*c*) **10.** (*d*) **11.** (*c*) **12.** (*i*) – (*c*), (*ii*) – (*c*), (*iii*) – (*c*), (*iv*) – (*a*), (*v*) – (*b*) **13.** (*a*)

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▶ Multiple Choice Questions (Type-II) ◀

14. Which of the following elements can show covalency greater than 4 ?
(*a*) Be (*b*) P
(*c*) S (*d*) B

15. Those elements impart colour to the flame on heating in it, the atoms of which require low energy for the ionisation (*i.e.*, absorb energy in the visible region of spectrum). The elements of which of the following groups will impart colour to the flame ?
(*a*) 2 (*b*) 13
(*c*) 1 (*d*) 17

16. Which of the following sequences contain atomic numbers of only representative elements ?
(*a*) 3, 33, 53, 87 (*b*) 2, 10, 22, 36
(*c*) 7, 17, 25, 37, 48 (*d*) 9, 35, 51, 88

17. Which of the following elements will gain one electron more readily in comparison to other elements of their group ?
(*a*) S (*g*) (*b*) Na (*g*)
(*c*) O (*g*) (*d*) Cl (*g*)

18. Which of the following statements are correct ?
(*a*) Helium has the highest first ionisation enthalpy in the periodic table.
(*b*) Chlorine has less negative electron gain enthalpy than fluorine.
(*c*) Mercury and bromine are liquids at room temperature.
(*d*) In any period, atomic radius of alkali metal is the highest.

19. Which of the following sets contain only isoelectronic ions ?
(*a*) $Zn^{2+}, Ca^{2+}, Ga^{3+}, Al^{3+}$ (*b*) $K^+, Ca^{2+}, Sc^{3+}, Cl^-$
(*c*) $P^{3-}, S^{2-}, Cl^-, K^+$ (*d*) $Ti^{4+}, Ar, Cr^{3+}, V^{5+}$

20. In which of the following options order of arrangement does not agree with the variation of property indicated against it ?
(*a*) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ (increasing ionic size)
(*b*) B < C < N < O (increasign first ionisation enthalpy)
(*c*) I < Br < Cl < F (increasing electron gain enthalpy)
(*d*) Li < Na < K < Rb (increasing metallic radius)

21. Which of the following have no unit ?
(*a*) Electronegativity
(*b*) Electron gain enthalpy
(*c*) Ionisation enthalpy
(*d*) Metallic character

22. Ionic radii vary in
(*a*) inverse proportion to the effective nuclear charge.
(*b*) inverse proportion to the square of effective nuclear charge.
(*c*) direct proportion to the screening effect.
(*d*) direct proportion to the square of screening effect.

23. An element belongs to 3rd period and group-13 of the periodic table. Which of the following properties will be shown by the element ?
(*a*) Good conductor of electricity
(*b*) Liquid, metallic
(*c*) Solid, metallic
(*d*) Solid, non-metallic.

Answers

14. (*b*, *c*) **15.** (*a*, *c*) **16.** (*a*, *d*) **17.** (*a*, *d*) **18.** (*a*, *c*) **19.** (*b*, *c*)
20. (*b*, *c*) **21.** (*a*, *d*) **22.** (*a*, *c*) **23.** (*a*, *c*)

Matching Type Questions

24. Match the correct atomic radius with the element :

Element	*Atomic radius (pm)*
(*i*) Be	(A) 74
(*ii*) C	(B) 88
(*iii*) O	(C) 111
(*iv*) B	(D) 77
(*v*) N	(E) 66

25. Match the correct ionisation enthalpies and electron gain enthalpies of the following elements :

Elements	ΔH_1	ΔH_2	$\Delta_{eg}H$
(*i*) Most reactive non-metal	(A) 419	3051	– 48
(*ii*) Most reactive metal	(B) 1681	3374	– 328
(*iii*) Least reactive element	(C) 738	1451	– 40
(*iv*) Metal forming binary halide	(D) 2372	5251	+ 48

26. Electronic configurations of some elements are given in Column I and their electron gain enthalpies are given in Column II. Match the electronic configuration with electron gain enthalpy.

Column (I) *Electronic configuration*	*Column (II)* *Electron gain enthalpy / kJ mol^{-1}*
(*i*) $1s^2 2s^2 2p^6$	(A) – 53
(*ii*) $1s^2 2s^2 2p^6 3s^1$	(B) – 328
(*iii*) $1s^2 2s^2 2p^5$	(C) – 141
(*iv*) $1s^2 2s^2 2p^4$	(D) + 48

Answers

24. (*i*) – (C), (*ii*) – (D), (*iii*) – (E), (*iv*) – (B), (*v*) – (A);
25. (*i*) – (B), (*ii*) – (A), (*iii*) – (D), (*iv*) – (C);
26. (*i*) – (D), (*ii*) – (A), (*iii*) – (B), (*iv*) – (C);

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Assertion Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

27. Assertion (A) : Generally, ionisation enthalpy increases from left to right in a period.

Reason (R) : When successive electrons are added to the orbitals in the same principal quantum level, the shielding effect of inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus.

(*a*) Assertion is correct statement and reason is wrong statement.

(*b*) Assertion and reason both are correct statement and reason is correct explanation of assertion.

(*c*) Assertion and reason both are correct statements.

(*d*) Assertion is wrong statement and reason is correct statement.

28. Assertion (A) : Boron has a smaller first ionisation enthalpy than beryllium.

Reason (R) : The penetration of a 2*s* electron to the nucleus is more than the 2*p* electron hence 2*p* electron is more shielded by the inner core of electrons than the 2*s* electrons.

(*a*) Assertion and reason both are correct statement but reason is not correct explanation for assertion.

(*b*) Assertion is correct statement but reason is wrong statement.

(*c*) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(*d*) Assertion and reason both are wrong statements.

29. Assertion (A) : Electron gain enthalpy becomes less negative as we go down a group.

Reason (R) : Size of the atom increases on going down the group and the added electron would be farther from the nucleus.

(*a*) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(*b*) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(*c*) Assertion and reason both are wrong statements.

(*d*) Assertion is wrong statement but reason is correct statement.

Answers

27. (*b*) **28.** (*c*) **29.** (*b*)

Hints & Explanations for *Difficult Objective Type Questions*

Multiple Choice Questions

A. Topicwise Multiple Choice Questions

A3. (*d*) : $3(1s^2 2s^1)$, $12(1s^2\ 2s^2\ 2p^6\ 3s^2)$ have electron in outermost *s*– subshell.

A5. (*c*) : *d*-block elements have maximum tendency to form complexes.

A6. (*d*) : The statements (*a*), (*b*) and (*c*) are correct but statement (*d*) is incorrect because it belongs to 7th period (outermost shell).

A7. (*c*) : Mt : [Rn] $5f^{14}\ 6d^7\ 7s^2$: *d*-block because the outer most electron is in *d*-subshell.

A8. (*a*) : All *p*-block elements have 6 elements in a period.

A9. (*c*) : The elements having similar valence electronic configuation belong to same group of the periodic table. Therefore, A and B having 3 electrons in the valence shell belong to same group.

A13. (*a*) : P^{3-}, S^{2-} and Cl^- have same number of electrons (18) and size decreases as nuclear charge increases.

$$Cl^- < S^{2-} < P^{3-}$$

A17. (*c*) : It corresponds to Cl and has largest negative electron gain enthalpy.

A28. (*c*) : $Li\,(g) + I.E \longrightarrow Li^+(g) + e^-(g)$

Moles of Li in 7 mg = $\frac{7 \times 10^{-3}}{7} = 1 \times 10^{-3}$ mol

Amount of energy needed to convert 1×10^{-3} mol of Li atoms

$520 \times 10^3\ J \times 1 \times 10^{-3} = 520J$

A33. (*d*) : Amount of energy released for 1×10^6 atoms

$= 4.9 \times 10^{-13}$ J

Amount of energy released for 6.022×10^{23} (1 mol) atoms

$$= \frac{4.9 \times 10^{-13}}{1 \times 10^6} \times 6.022 \times 10^{23}$$

$= 29.5 \times 10^4 J = 295\ kJ\ mol^{-1}$

A34. (*c*) : Chlorine has the highest negative electron gain enthalpy. It belongs to period 3 and group 17.

A35. (*c*) : The fourth ionisation enthalpy is abruptly increased, which means that the electron is removed from noble gas configuration.

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B. *mcq from competitive examinations*

B5. (*c*) : 117 : [Rn] $5f^{14}6d^{10}7s^27p^5$: It will belong to halogen family.

B7. (*d*) : Group 17 > Group 16
Group 17 → Cl > F > Br > I
Group 16 → S > Se > Te > Po > O
∴ The correct order is :
O < S < F < Cl

B8. (*a*) : For isoelectronic species, smaller the positive charge on the cation, larger is the ionic radius.

B11. (*c*) : For option (*a*), the order is $H^- > H > H^+$, for option (*b*) the order is $O^{2-} > F^- > Na$; for option (*d*), the order is $N^{3-} > Mg^{2+} > Al^{3+}$.
Hence, (*c*) is correct: $O^{2-} > F^- > Na^+$ correct.

B14. (*a*) : With increase in nuclear charge, size decreases in isoelectronic species.
Ca^{2+} (Z = 20) < K^+ (Z = 19) < Ar (Z = 18)

B15. (*a, d*) : The correct order of increasing –ve electron gain enthalpy value among halogens is
I < Br < F < Cl option (*a*) is wrong.
Nitrogen has the electronic configuration, $2s^22p^3$ (i.e., half filled 2*p* configuration). Therefore, it has higher first ionization enthalpy than oxygen. Option (*d*) is wrong. The correct order is : B < C < O < N.

B16. (*a*) : Electronic configuration of the element, Z = 114 is $[Rn]^{86}\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^2$
It belongs to group 14 *i.e.* carbon family.

B17. (*d*) : X having ground state configuration $1s^22s^22p^3$ is N and its valency is –3.
Formula: $Mg^{+2}X^{-3}$ or Mg_3X_2

B18. (*b*) : Nitrogen has half filled stable configuration so that its ionization enthalpy is greater than that of oxygen. So, correct order of increasing first ionization enthalpy is :
B < C < O < N

B22. (*c*) : The configuration corresponds to that of Cl, which has the highest negative electron gain enthalpy.

B23. (*e*) : Alkali metals have lowest value of ionisation enthalpy in a period. On moving down the group from top to bottom, the ionisation enthalpy decreases. Hence from the graph, M has least ionisation enthalpy.

B24. (*a*) : On moving from left to right in a period, ionisation enthalpy increases due to increase in effective nuclear charge. But electronic configuration of oxygen is unexpectedly lower than that of nitrogen. This is because nitrogen has stable half filled electronic configuration ($1s^22s^22p^3$).

B25. (*b*) : Ionic radius increases from top to bottom and decreases on moving from left to right in a periodic table.

B29. (*c*) : The most reactive metal will be the one having lowest ionisation enthalpy and the least reactive non-metal will be the one having lowest or positive electron gain enthalpy.

B30. (*b*) : For isoelectronic ions, the ionic radius decreases with increase in nuclear charge.
Correct order is :
$O^{2-}(+8) > F^-(+9) > Na^+(+11) > Mg^{2+}(+12) > Al^{3+}(+13)$

B31. (*b*) : The configurations of atoms and ions after removing one electron are :

Li	:	$1s^22s^1$	Li^+	:	$1s^2$
Be	:	$1s^22s^2$	Be^+	:	$1s^22s^1$
B	:	$1s^22s^22p^1$	B^+	:	$1s^22s^2$
C	:	$1s^22s^22p^2$	C^+	:	$1s^22s^22p^1$

Hence the order of IE_2 is Li > B > C > Be

B32. (*b*) : The order of size is : $Na^+ < F^- < Cl^- < S^{2-}$

B33. (*d*) : Size decreases down the group.

B34. (*c*) : Phosphorus belongs to group 15 and third period.

B44. (*d*) : Larger is the negative charge and size of anion, higher is its polarising power.

B46. (*b*) : In isoelectronic ions, with increase in nuclear charge, size decreases,
Therefore, $Ca^{2+} < K^+ < Cl^- < S^{2-}$.

B47. (*c*) : Isoelectronic species are those which have same number of electrons. K^+, Ca^{2+}, Sc^{3-} and Cl^- have 18 electrons.

B48. (*d*) : Among these neon has the highest positive electron gain enthalpy.

B49. (*d*) : In general, ionization enthalpy decreases from top to bottom (Ba < Ca), (Se < S) and increases from left to right in a period (Ca < Se), (S < Ar). Therefore, correct order of increasing first ionization enthalpy is :
Ba < Ca < Se < S < Ar

B50. (*c*) : Electron gain enthalpy = – Ionisation potential
∴ = – 5.1 eV

B54. (*a*) : With increase in nuclear charge, size decreases in isoelectronic ions.
$N^{3-}(Z=7) > O^{2-}(Z=8) < F^-(Z=9)$

B55. (*d*) : The outer electronic configuration of the element 'X' is : $3d^{10}\ 4s^2\ 4p^3$. It has half filled *p*-orbitals and completely filled *s*-and *d*-orbitals.

B56. (*d*) : Sc has the highest ionization enthalpy. This is because, it is difficult to remove an electron from 4*s* orbital of Sc as compared to 3*s* orbital of Na due to poor shielding of *d*-orbitals and high effective nuclear charge.

B57. (*a*) : F has the highest negative electron gain enthalpy.

B59. (*a*) : Mg^{2+}, Na^+, O^{2-} and F^-, all have 10 electrons each and are therefore, isoelectronic.

B61. (*c*) : For isoelectronic ions, higher the positive charge, smaller will be the ionic radius.

B62. (*c*) : Noble gases have high ionization potential.

B63. (*d*) : In general, electrons are added one at a time to the $(n-1)d$ orbitals in transition elements. However, because of extra stability of d^5 and d^{10} configurations, two electrons appear to have entered the *d*-subshell due to shifting of one electron from *ns* to $(n-1)d$ orbital.

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B64. (*c*): C N Si < C ; Si < P ; C < N ; P < N
2.5 3.0
Si P
1.9 2.2
So, correct order is Si < P < C < N

C. *mcq with more than one correct answer*

C1. (*a*,*c*) : (*a*) all have 10 electrons, (*c*) all have 18 electrons.

C2. (*c*,*d*) : 14 elements of 6th period are called lanthanoids, 4th period begins with potassium.

C3. (*b*,*c*) : O > S and N > O.

C5. (*a*,*b*) : C < N > O, $F^- > Na^+ > Mg^{2+}$

C6. (*b*,*c*) : These belong to *f*-block

NCERT Exemplar Problems: MCQs Type-I

1. (*b*) : Amongst isoelectronic ions, ionic radii decrease with increase in nuclear charge :
$Mg^{2+}(12) < Na^+(11) < F^-(10) < O^{2-}(8)$

2. (*d*) : Actinoids are elements with Z = 90 – 103. Therefore, terbium (Z = 65) is not an actinoid.

4. (*a*) : $Na(3s^1) < Mg(3s^2) > Al(3s^23p^1) < Si(3s^23p^2)$

NCERT Exemplar Problems: MCQs Type-II

14. (*b*, *c*) : P and S have *d*-orbitals in their valence shell and therefore, can accommodate more than 8 electrons in their respective valence shells. Hence they show covalency more than 4.

15. (*a*, *c*) : The elements of group 1(alkali metals) and group 2(alkaline earth metals) have low ionization enthalpies. Therefore, they impart colour to flame.

16. (*a*, *d*) : Elements of *s*- and *p*-blocks are called representative elements.

17. (*a*, *d*) : Chlorine has highest tendency to gain an electron and its electron gain enthalpy (–ve) is high. O and S belong to group 16 but S has larger tendency to accept electron.

19. (*b*, *c*) : (*a*) Zn^{2+} (30 – 2 = 28), Ca^{2+}(20 – 2 = 18), Ga^{3+} (31–3=28), Al^{3+}(13–3=10) are not isoelectronic.

(*b*) K^+ (19–1=18), Ca^{2+}(20–2=18), Se^{3+} (21–3=18), Cl^-(17 + 1 = 18) are isoelectronic.

(*c*) P^{3-} (15+3=18), S^{2-} (16+2=18), Cl^- (17+1=18), K^+(19 – 1 = 18) are isoelectronic.

(*d*) Ti^{4+} (22 – 4 = 18), Ar (18), Cr^{3+}(24 – 3 = 21), V^{5+} (23 – 5 = 18) are not isoelectronic.

20. (*b*, *c*) : For (*b*) correct order is B < C < O < N
For (*c*) correct order is I < Br < F < Cl

21. (*a*, *d*) : Electronegativity and metallic character has no units.

22. (*a*, *c*) : Ionic radius decreases as effective nuclear charge increases.
Ionic radius increases as the screening effect increases.

23. (*a*, *c*) : The elements which belong to 3rd period and group 13 is aluminium. It is solid, metallic and good conductor of electricity.

NCERT Exemplar Problems: Matching Type

24. As we move from left to right in a period, the atomic radius decreases. Thus, Be > B > C > N > O.

25. (*i*) Most reactive non-metals have high Δ_iH_1 and Δ_iH_2 and negative $\Delta_{eg}H$. Therefore, the element is B.

(*ii*) Most reactive metals have low Δ_iH_1 and high Δ_iH_2 (because the second electron has to be removed from noble gas configuration) and small $\Delta_{eg}H$ value. Therefore, the element is A.

(*iii*) Noble gases are least reactive elements and have very high Δ_iH_1 and Δ_iH_2 and have positive $\Delta_{eg}H$. Therefore, the element is D.

(*iv*) Metals forming binary halides are rare earth metals. They have Δ_iH_1 and Δ_iH_2 values slightly higher than those of most reactive metals (such as A) and have less negative $\Delta_{eg}H$ values. Therefore, the element is C.

26. (*i*) This configuration corresponds to noble gas (neon). Since noble gases have positive $\Delta_{eg}H$ values, therefore, electronic configuration A corresponds to element D.

(*ii*) The electronic configuration corresponds to alkali metal (potassium). Since alkali metals have low $\Delta_{eg}H$ values, therefore, electronic configuration (*ii*) corresponds to element A.

(*iii*) This electronic configuration corresponds to halogen (fluorine). Since halogens have high negative $\Delta_{eg}H$ values, therefore, the electronic configuration (*iii*) corresponds to element B.

(*iv*) This electronic configuration corresponds to oxygen family (oxygen). Since oxygen has $\Delta_{eg}H$ value less negative than halogens, therefore, the electronic configuration (IV) corresponds to element C.

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Unit Practice Test

for Board Examination

Time Allowed: 1 Hr. ***Maximum Marks: 25***

1. Which among N, O and F has lowest ionization enthalpy? (1)

2. Which of two F or Cl has higher negative electron gain enthalpy? (1)

3. Which among I, I^+ and I^- has smallest size ? (1)

4. To which block do the elements with atomic numbers 28 and 32 belong? (1)

5. Arrange the elements : B, Al, Mg and K in the decreasing order of metallic character. (1)

6. How would you account for the fact that the first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium? (2)

7. Would you expect the second electron gain enthalpy of oxygen as positive, more negative or less negative than the first. Explain (2)

8. Which of the following pairs of elements would have more negative electron gain enthalpy?

(*i*) O or F (*ii*) Cl or F

(*iii*) N or P (*iv*) B or Al (2)

9. Give the general electronic configurations of

(*a*) *p*-block (*b*) actinoids

10. Among the elements of second and third period, predict the following :

(*i*) element (except noble gases) having largest ionization enthalpy and element having lowest ionisation enthalpy.

(*ii*) element (except noble gases) having smallest atomic size and element having largest atomic size.

(*iii*) elements having six electrons in the valence shell. (3)

11. Consider the ground state electronic configuration given below :

A : $1s^2 2s^2 2p^5$ B : $1s^2 2s^2 2p^4$

C : $1s^2 2s^2 2p^6 3s^2\ 3p^5$ D : $1s^2 2s^2 2p^6 3s^1$

E : $1s^2 2s^2 2p^4$

Which of the above configuration corresponds to element having

(*a*) maximum negative electron gain enthalpy?

(*b*) largest atomic size.

(*c*) having highest ionisation enthalpy. (3)

12. Explain the following :

(*a*) Oxygen has lower $\Delta_i H$ than N and F.

(*b*) Elements in the same group have similar physical and chemical properties.

(*c*) Size of an anion is larger than the corresponding atom but the size of cation is smaller than the corresponding atom. (3)

13. (*a*) What is the basic difference in approach between the Mendeleev's periodic law and modern periodic law ?

(*b*) Explain the variation in acidic and basic character of oxides of second row elements.

(*c*) Account for the variation in metallic or non-metallic character in third row elements. (5)

To check your performance, see HINTS and SOLUTIONS to some questions at the end of Part I of the book.

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UNIT 4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

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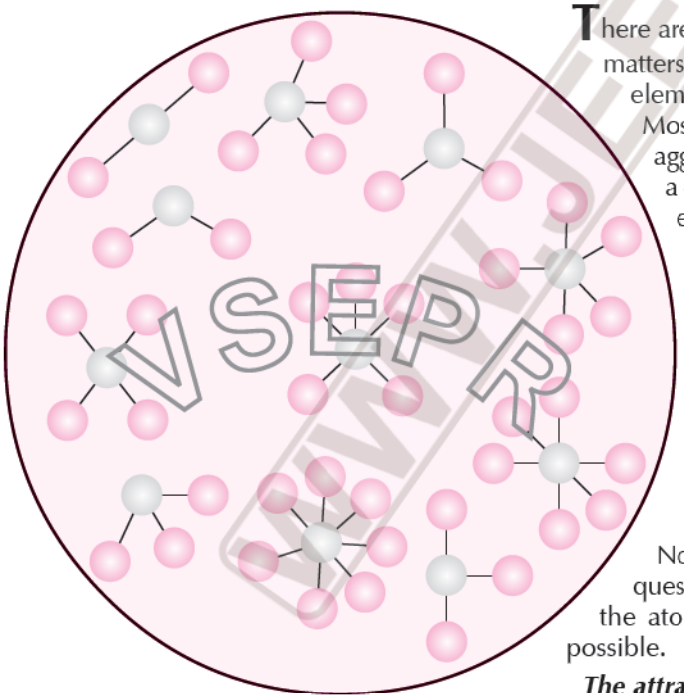

There are about 118 different kinds of elements which constitute all matters. It is well known fact that except for noble gases, no other element exists as independent atoms under ordinary conditions. Most of these atoms exist as molecules which are cluster or aggregates of atoms or ions of same or different elements having a distinct existence and its own characteristic properties. The existence of a large number of molecules or compounds raises many questions, such as :

(*i*) Why do atoms combine?
(*ii*) Why do certain atoms combine whereas others do not?
(*iii*) What is the nature of the forces which hold the atoms together in molecules?
(*iv*) Why do atoms have fixed combining capacity?
(*v*) Why do molecules possess definite shapes?

In Unit 2, we have studied the structure of an atom. Now, we proceed to seek answers to the above important questions, laying stress on the nature of links or bonds between the atoms and the forces which make such linkages or bonds possible.

The attractive force which holds together the constituent particles (atoms, ions or molecules) in a chemical species is known as **chemical bond.**

WHY DO ATOMS COMBINE ?

A number of attempts were made to explain the formation of chemical bonds between atoms in terms of electrons. In 1916, Kossel and Lewis succeeded independently in giving first successful explanation about the cause of combination between atoms based upon the understanding of electronic configuration of noble gases.

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Table 1. Electronic configurations of noble gases.

Noble gas	Atomic number	Electronic configuration	Configuration of valence shell
Helium (He)	2	$1s^2$	$1s^2$
Neon (Ne)	10	$1s^2, 2s^2\ 2p^6$	$2s^2 2p^6$
Argon (Ar)	18	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6$	$3s^2 3p^6$
Krypton (Kr)	36	$1s^2, 2s^2 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6$	$4s^2 4p^6$
Xenon (Xe)	54	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2\ 4p^6\ 4d^{10}, 5s^2\ 5p^6$	$5s^2 5p^6$
Radon (Rn)	86	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6 4d^{10}\ 4f^{14}, 5s^2\ 5p^6\ 5d^{10}, 6s^2 6p^6$	$6s^2\ 6p^6$

(*i*) **Tendency to acquire noble gas configuration or octet rule.**

It has been observed that atoms of noble gases have little or no tendency to combine with each other or with atoms of other elements. This means that these atoms must be having stable electronic configurations. The electronic configurations of these elements are given in Table 1.

From Table 1, we find that the atoms of all noble gases (with the exception of helium) have eight electrons in their valence shell. Helium on the other hand, has two electrons in its valence shell (first energy shell) because the first energy shell ($n = 1$) cannot have more than two electrons. The electronic configuration of the valence shell for all noble gas atoms except helium can be expressed as $\boldsymbol{ns^2\ np^6}$ (for helium, $1s^2$) and this represents the stable configuration and *corresponds to maximum stability*. Due to the stable configuration, the noble gas atoms neither have any tendency to gain nor lose electrons and, therefore, **their combining capacity (or valency) is zero**.

All atoms other than noble gases have less than eight electrons in their outermost shells. In other words, the outermost shells of these atoms do not have stable configurations. Therefore, they combine with each other or with other atoms to achieve stable noble gas electronic configurations ($ns^2\ np^6$ or $1s^2$). To a large extent, the elements undergo electronic re-arrangements to attain stable noble gas configurations. Thus,

the tendency or urge of atoms of various elements to attain stable configuration of eight electrons in their valence shells, *is the* **cause of chemical combination.**

The ***principle of attaining maximum of eight electrons in the valence shell of atoms,*** *is called* **octet rule.**

However, it may be noted that for hydrogen and lithium atoms, the stable configuration means two electrons which corresponds to the nearest noble gas helium.

(*ii*) **Tendency to acquire minimum energy and stability.**

According to modern view, the atoms combine to form chemical bonds to acquire a state of minimum energy. As we know, every system in the universe has a natural tendency to attain a state of minimum energy. The state of minimum energy corresponds to state of maximum stability. Hence, the atoms combine with each other, *only if the process leads to lowering of energy.* If there is no fall in potential energy of the system, no bonding is possible.

LEWIS SYMBOLS

In the formation of a molecule, only the outer shell electrons take part in chemical combination. Therefore, these are also called ***valence shell electrons.*** The inner shell electrons are well protected and, therefore, they generally do not take part. G.N. Lewis, an American chemist, introduced simple notations to represent valence electrons in an atom. These notations are called *Lewis symbols* or *electron dot symbols.*

Lewis symbols or electron dot symbols

According to Lewis notations, the symbol of the element represents the whole of the atom except the valence electrons (*i.e.*, nucleus and the electrons in the inner energy shells). The valence electrons are represented by placing dots (·) or crosses (×) around the symbol. For example, the Lewis symbols for the atoms of second period are :

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Similarly, the Lewis symbols for the elements of third period are :

$\dot{Na}$, $\dot{Mg}$, $\dot{Al}\cdot$, $\cdot\dot{Si}\cdot$, $\cdot\ddot{P}\cdot$, $\cdot\ddot{S}:$, $\cdot\ddot{Cl}:$, $:\ddot{Ar}:$

Significance of Lewis Symbols

(*i*) The Lewis symbols indicate the number of electrons in the outermost or valence shell.

(*ii*) These help to predict the common or **group valence** of the element. For example, lithium has one electron in valence shell and it can involve this electron in chemical combination process (by losing or sharing) and it is therefore, *monovalent;* beryllium has 2 electrons for participating in chemical combination and is *divalent.* Similarly, B and C are *trivalent* and *tetravalent* because they have three and four electrons respectively. Thus, for Li, Be, B and C, the number of electrons also indicates the common valence of these elements. However, *the common valence for N, O, F and Ne is equal to eight minus the valence electrons.* For example, for N it is 3, for O it is 2, for F it is one and for Ne it is 0. Thus,

the common valence of an element is either equal to number of dots in the Lewis symbol or it is equal to 8 minus the number of dots.

SOLVED EXAMPLES

Example 1.

Write Lewis dot symbols for the following atoms and ions :

(i) O (ii) O^{2-} (iii) Mg^{2+} (iv) P^{3-} (v) Br

Solution: Lewis dot symbols are :

(*i*) $\cdot\ddot{O}\cdot$ (*ii*) $:\ddot{O}:^{2-}$ (*iii*) $:\ddot{Mg}:^{2+}$ or Mg^{2+}

(*iv*) $:\ddot{P}:^{3-}$ (*v*) $:\ddot{Br}:$

Example 2.

Write Lewis dot symbols for the following atoms and ions :

(i) S and S^{2-} (ii) P and P^{3-}
(iii) Al and Al^{3+} (iv) H and H^-
(v) Na ans Na^+ ***N.C.E.R.T.***

Solution: Lewis dot symbols are :

(*i*) $:\ddot{S}\cdot$ and $:\ddot{S}:^{2-}$ (*ii*) $\cdot\ddot{P}\cdot$ and $:\ddot{P}:^{3-}$

(*iii*) $\cdot\dot{Al}\cdot$ and Al^{3+} (*iv*) $\dot{H}$ and $H:^-$

(*v*) $\dot{Na}$ and Na^+

Practice Problems

1. Write Lewis dot symbols for atoms of the following elements :
Mg, Na, B, O, N, Br

2. Write Lewis dot symbols for the following ions :
Li^+, Cl^-, O^{2-}, Mg^{2+} and N^{3-}

3. Draw Lewis dot symbols for the following elements:
(*i*) Magnesium (*ii*) Phosphorus
(*iii*) Chlorine (*iv*) Boron
(*v*) Xenon (*vi*) Silicon

4. Draw Lewis dot symbols for the elements of third period of the periodic table.

Answers to Practice Problems

1. $\dot{Mg}\cdot$, $\dot{Na}$, $\cdot\dot{B}\cdot$, $\cdot\ddot{O}\cdot$, $\cdot\ddot{N}\cdot$, $\cdot\ddot{Br}\cdot$

2. Li^+, $:\ddot{Cl}:^-$, $:\ddot{O}:^{2-}$, Mg^{2+} $:\ddot{N}:^{3-}$

3. (*i*) $\dot{Mg}\cdot$ (*ii*) $\cdot\ddot{P}\cdot$ (*iii*) $:\ddot{Cl}\cdot$

(*iv*) $\cdot\dot{B}\cdot$ (*v*) $:\ddot{Xe}:$ (*vi*) $\cdot\dot{Si}\cdot$

OCTET RULE AND MODES OF CHEMICAL COMBINATION

In the light of octet rule, W. Kossel and G. N. Lewis, in 1916, developed an important theory of chemical combination between atoms known as *electronic theory of chemical bonding.* According to this, *atoms achieve the stable octet when they are linked by chemical bonds.* In other words, atoms combine to have an octet in their valence shells (stable noble gas configurations). They do so either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons. Thus, *atoms combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have octet in their valence shells.* This is called **octet rule**.

For example, sodium, magnesium and aluminium in the third period of the periodic table lose electrons with the formation of positive ions (cations) that have the same electronic configuration as neon ($1s^2 2s^2 2p^6$)

$$\underset{1s^2 2s^2 2p^6 3s^1}{\dot{Na}} \longrightarrow \underset{1s^2 2s^2 2p^6}{Na^+} + e^-$$

$$\underset{1s^2 2s^2 2p^6 3s^2}{\cdot\dot{Mg}} \longrightarrow \underset{1s^2 2s^2 2p^6}{Mg^{2+}} + 2e^-$$

$$\underset{1s^2 2s^2 2p^6 3s^2 3p^1}{\cdot\dot{Al}\cdot} \longrightarrow \underset{1s^2 2s^2 2p^6}{Al^{3+}} + 3e^-$$

The dots with these symbols represent electrons in the valence shell. On the other hand, oxygen and fluorine can acquire noble gas configuration by easily gaining electrons to form negative ions (anions).

$$\underset{1s^2 2s^2 2p^4}{:\ddot{O}:} + 2e^- \longrightarrow \underset{1s^2 2s^2 2p^6}{:\ddot{O}:^{2-}}$$

$$\underset{1s^2 2s^2 2p^5}{:\ddot{F}:} + e^- \longrightarrow \underset{1s^2 2s^2 2p^6}{:\ddot{F}:^-}$$

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In relation to chemical bonding, W. Kossel drew attention to the following facts of the periodic table :

(*i*) In the periodic table, the highly electronegative halogens are placed on the right and the highly electropositive alkali metals are present on the extreme left. These two families are separated by noble gases.

(*ii*) Halogens gain an electron to form a negative ion while alkali metals lose an electron to form a positive ion. Therefore, these ions are formed by the gain or loss of electron by their respective atoms.

(*iii*) The negative and positive ions so formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has a duplet of electrons) have a stable outer electronic configuration of eight (octet) electrons, $ns^2 np^6$.

This is *the basis of formation of chemical bonds.*

The atoms can also acquire noble gas configurations by sharing with other atoms. Therefore, there are two main types of bonds. These are :

(*i*) *Ionic bond* and

(*ii*) *Covalent bond.*

IONIC OR ELECTROVALENT BOND

When a bond is formed by the transference of one or more valence electrons of one atom to the other atom so as to complete their outermost octets and acquire stable nearest noble gas configurations, the bond formed is called ***electrovalent bond or ionic bond.***

In this type of bonding, one atom completes its octet and acquires noble gas configuration by losing the electrons and other by gaining the electrons. The atom which loses the electrons acquires a positive charge and the other which gains the electrons acquires a negative charge. These two oppositely charged ions, thus formed, come closer due to electrostatic forces of attraction and form an ionic bond. Thus,

the electrostatic force of attraction which holds the oppositely charged ions together is known as ***ionic bond or electrovalent bond.***

The compounds containing ionic or electrovalent bonds are called ***ionic or electrovalent compounds.***

Let us illustrate the formation of ionic bond by considering the example of sodium chloride. Sodium atom ($1s^2\ 2s^2\ 2p^6\ 3s^1$) has only one electron in the valence shell and by losing this electron, it can acquire stable electronic configuration of neon ($1s^2\ 2s^2\ 2p^6$).

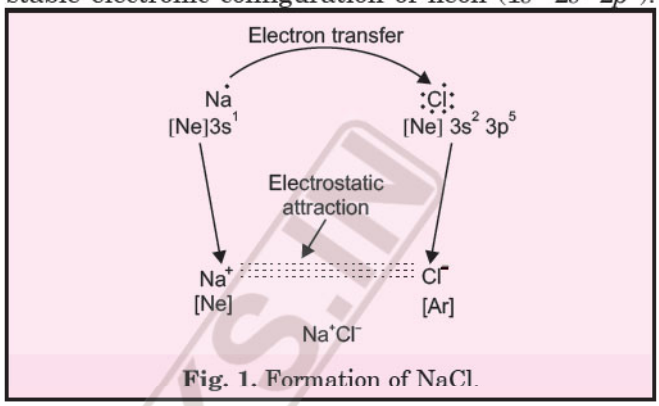


Fig. 1. Formation of NaCl.

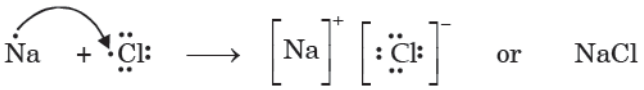
On the other hand, chlorine atom ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$) has seven electrons in its valence shell and needs only one electron to complete its octet. Thus, both the atoms can complete their octets if sodium atom gives one electron to chlorine atom. This tendency is responsible for bonding between sodium and chlorine atoms. Therefore, sodium gives one electron and becomes positively charged Na^+ ion, while chlorine takes up the electron and becomes negatively charged, Cl^- ion. These two ions are then held together by electrostatic forces of attraction which constitute the ionic bond. In terms of Lewis structure, the ionic bond between Na and Cl may be represented as:

$$\underset{[Ne]\ 3s^1}{Na} \longrightarrow \underset{[Ne]}{Na^+} + e^-$$

$$\underset{[Ne]\ 3s^2 3p^5}{Cl + e^-} \longrightarrow \underset{[Ne]\ 3s^2\ 3p^6 \text{ or } [Ar]}{Cl^-}$$

$$Na^+ + Cl^- \longrightarrow \underset{\text{Ionic compound}}{Na^+\ Cl^- \text{ or } NaCl}$$

Formation of sodium chloride may also be shown as :



Formation of CaF_2. The electronic configurations of calcium and fluorine atoms are

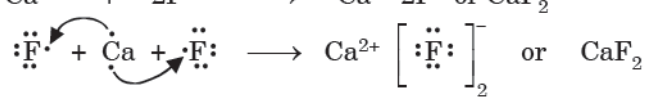
Ca (Z = 20) : [Ar] $4s^2$, F (Z = 9) : [He] $2s^2 2p^5$

In the formation of calcium fluoride, calcium loses its both the valence electrons to two fluorine atoms each of which is in need of one electron. This results in the formation of Ca^{2+} ion and two F^- ions. Each of these ions acquires noble gas configuration. One Ca^{2+} and two F^- ions form bonds to give calcium fluoride. This may be represented as :

$$\underset{[Ar]\ 4s^2}{Ca} \longrightarrow \underset{[Ar]}{Ca^{2+}} + 2e^-$$

$$\underset{[He]\ 2s^2\ 2p^5}{F + e^-} \longrightarrow \underset{[He]2s^2\ 2p^6 \text{ or } [Ne]}{F^-}$$

$$Ca^{2+} + 2F^- \longrightarrow Ca^{2+}\ 2F^- \text{ or } CaF_2$$



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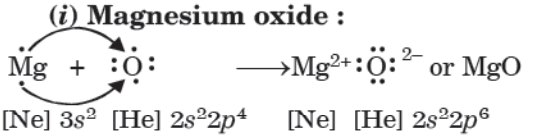
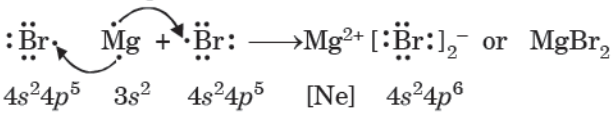
In the formation of electrovalent bond, the number of electrons lost or gained by an atom is called its ***electrovalence*** *or* ***electrovalency***. It is also equal to the number of unit charges on the ion. For example, sodium is assigned a positive electrovalence of one, calcium is assigned a positive electrovalence of two. Similarly, chlorine and fluorine both are assigned a negative electrovalence of one. Atoms that readily lose electrons are called **electropositive** while those which readily gain electrons are called **electronegative**.

Some more examples of formation of ionic bonds are:

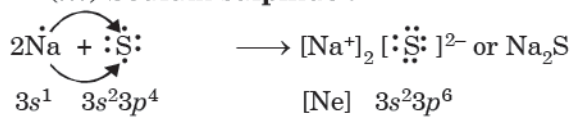
(*i*) Magnesium oxide :



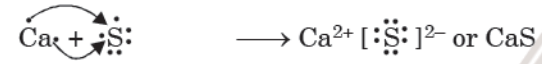
(*ii*) Magnesium bromide :



(*iii*) Sodium sulphide :



(*iv*) Calcium sulphide



FORMATION OF IONIC BOND

The formation of ionic compounds would primarily depend upon:

- The ease of formation of positive and negative ions from the respective neutral atoms.
- The arrangement of positive and negative ions in the solid. This is also called the **lattice** of the crystalline compound.

Factors on which the Formation of Ionic Bonds depend

The tendency of atoms to form ionic bonds between them depends upon the following factors :

1. Low ionization enthalpy. The ease with which an atom can lose electrons depends upon its *ionization enthalpy.* The **ionization enthalpy** is the *amount of energy required to remove the most loosely bound electron from an isolated gaseous atom to form a positive ion.*

$$M(g) \longrightarrow M^+(g) + e^- \quad \text{Ionization enthalpy}$$

Lesser the ionization enthalpy of an atom, the greater is the ease of losing the valence electron. Therefore, in general, *metals which have low ionization enthalpy values,* have greater tendency to form ionic bonds. For example, alkali and alkaline earth metals which have relatively low ionization enthalpies, generally form ionic compounds.

2. High electron gain enthalpy. The tendency of an atom to gain electrons depends upon its *electron gain enthalpy.* The **electron gain enthalpy** is the *amount of energy released when an electron is added to an isolated gaseous atom to form a negative ion.*

$$X(g) + e^- \longrightarrow X^-(g) \quad \text{Electron gain enthalpy}$$

Higher the value of negative electron gain enthalpy, greater will be the ease of formation of anion. Therefore, in general, *the elements which have high gain enthalpy values form ionic compounds*. For example, halogen and oxygen group elements mostly form **ionic compounds**.

3. High lattice enthalpies. The formation and strength of an ionic bond also depend upon the electrostatic force of attraction between oppositely charged ions. Due to the strong electrostatic attraction between the ions, formation of the crystal results in release of energy. *The amount of energy released when free ions combine together to form one mole of a crystal* is called **lattice enthalpy** (U).

$$M^+(g) + X^-(g) \longrightarrow \underset{\substack{\text{Ionic compound}\\(1\ \text{mole})}}{MX(s)} + \text{Lattice enthalpy}$$

Higher the value of lattice enthalpy, greater will be the ease of formation of the ionic compound.

The ionization process is always endothermic (absorbs energy) while electron gain enthalpy process may be exothermic (releases energy) or endothermic (absorbs energy). Lattice enthalpy is exothermic (releases energy). Now, if the net effect of the above three factors is the release of energy, then ionic bond will be formed. This is in accordance with the general observation that only those processes occur in which there is decrease of energy.

Let us consider these steps for NaCl :

(*i*) $Na(g) \longrightarrow Na^+(g) + e^-$

$\Delta_i H = 495.8\ kJ\ mol^{-1}$

(*ii*) $Cl(g) + e^- \longrightarrow Cl^-(g)$

$\Delta_{eg} H = -348.7\ kJ\ mol^{-1}$

(*iii*) $Na^+(g) + Cl^-(g) \longrightarrow Na^+Cl^-(s)$

$U = -788\ kJ\ mol^{-1}$

The ionic bond is formed because the energy released in step (*ii*) and (*iii*) is more than the energy required in step (*i*). As may be calculated from the above

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steps, 640.9 kJ mol^{-1} of energy is released and therefore, NaCl is formed. Thus, **a quantitative measure of the stability of an ionic compound is provided by its lattice enthalpy and not simply by achieving octet of electrons around the ionic species in the gaseous state**.

Thus, to **sum up,** the conditions for stable ionic bonding are :

(*i*) The ionisation enthalpy of atom forming the cation should be low.

(*ii*) The electron gain enthalpy of atom forming the anion should be highly negative.

(*iii*) Lattice enthalpy should be high.

LATTICE ENTHALPY OF IONIC CRYSTALS

The stability of ionic crystals is determined in terms of their lattice enthalpy. **Lattice enthalpy** is defined as

the amount of energy released when one mole of ionic crystal is formed from its constituent ions in the gaseous state.

The formation of one mole of the ionic solid from its constituent gaseous ions may be represented as :

$$M^+(g) + X^-(g) \longrightarrow MX(s);\ \Delta H = \text{Lattice enthalpy} = -U$$

The lattice enthalpy is expressed by U. The negative sign is used because energy is released in the process. Since ionic bond is formed as a consequence of electrostatic attractions between the oppositely charged ions, there is a considerable decrease of potential energy of the system. On the other hand, if one mole of solid ionic compound is broken into its constituent gaseous ions, energy will be needed which will be numerically equal to the lattice energy. Thus,

$$MX(s) \longrightarrow M^+(g) + X^-(g);\qquad \Delta H = +U$$

In this case, U has + ve sign because energy is absorbed in the process. Thus,

Lattice enthalpy may also be defined as: ***the energy required to completely separate one mole of a solid ionic compound into gaseous ionic constituents.***

It is obvious that if the compound is stable, a large amount of energy will be needed (numerically equal to lattice enthalpy). This means that *the higher the lattice enthalpy of an ionic compound, greater will be its stability.* The magnitude of lattice enthalpy gives an idea about the interionic forces. It depends upon the following factors :

(*i*) **Size of the ions.** Smaller the size of the ions, lesser is the internuclear distance. Consequently, the interionic attractions will be high and the lattice enthalpy will also be large. For example, ionic radius of K^+ (133 pm) is larger than that of Na^+ (95 pm), therefore, the lattice enthalpy of NaCl (758.7 kJ mol^{-1}) is greater than that of KCl (681.4 kJ mol^{-1}).

(*ii*) **Charge on the ions.** Larger the magnitude of charge on the ions, greater will be the attractive forces between the ions. Consequently, the lattice enthalpy will be high.

Lattice enthlpies of some ionic compounds are given in Table 2.

It is evident from the Table 2 that the lattice enthalpies of ionic solids are quite high. This is because of the strong electrostatic attractions between oppositely charged ions present in the solid. Since coulombic forces of attraction vary directly as the product of the charges, it follows that the higher the valency (charge) of the ions, the greater would be the lattice enthalpy of the ionic solid. Thus, lattice enthalpy increases as we move from uni-univalent ionic solids to uni-bivalent ionic solids and then to bi-bivalent ionic solids.

It may be noted that most of the ionic compounds have cations derived from metallic elements and anions from non-metallic elements. The ammonium ion, NH_4^+ (made up of two non-metallic elements) is an exception. It forms the cation of a number of ionic compounds.

Table 2. Lattice enthalpies of some ionic solids.

Uni-univalent solids		Bi-univalent solids		Bi-bivalent solids	
Ionic solid	**Lattice enthalpy (kJ mol^{-1})**	**Ionic solid**	**Lattice enthalpy (kJ mol^{-1})**	**Ionic solid**	**Lattice enthalpy (kJ mol^{-1})**
LiF	–1033	CaF_2	–2581	BeO	–3125
CsF	–748	$CaCl_2$	–2254	MgO	–3932
NaCl	–758	MgF_2	–2882	MgS	–3254
NaBr	–752	$MnCl_2$	–2525	ZnO	–4032
LiI	–140				
CsI	–601				
AgCl	–895				
AgI	–795				

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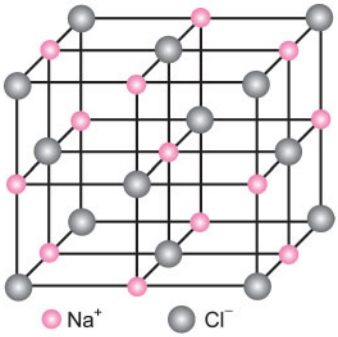
GENERAL PROPERTIES OF IONIC COMPOUNDS

The general properties of ionic compounds are :

1. Physical state. Ionic compounds usually exist in the form of crystalline solids. X-rays studies of these compounds show that these compounds do not exist



as independent molecules but exist in the form of ions. These ions are arranged in some definite geometric patterns to form the crystal lattice. For example, in NaCl crystal, each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions. ***The number of oppositely charged ions present as the nearest neighbours around an ion* is called its coordination number.** Thus, coordination number of Na^+ in NaCl ionic crystal is 6 and similarly, the coordination number of Cl^- ion in NaCl crystal is 6. The crystal structure of sodium chloride (called rock salt) is shown.

The geometric arrangement of different substances is different. It depends upon the size of the ions and the magnitude of the charges on the ions.

2. Melting and boiling points. Ionic compounds have high melting and boiling points. This is because the ions are held together by strong electrostatic forces of attractions and hence large amount of energy is required to break the crystal lattice. The variation in melting point depends upon the charges on the ions and ionic radii. The closer the ions in crystal, the larger will be the electrostatic forces of attraction and consequently, higher will be the melting point. For example, in case of sodium halides the melting points decrease from NaF to NaI : NaF (1270 K), NaCl (1073 K), NaBr (1023 K) and NaI (924 K).

3. Solubility. Ionic compounds are generally soluble in water and other polar solvents having high dielectric constants. This is due to larger electrostatic interactions between polar solvents and ions. However ionic compounds are insoluble in non-polar solvents.

4. Electrical conductivity. Ionic compounds are good conductors of electricity in the solution or in their molten states. In the solution or in their molten states, the ions become free to move. However, these do not conduct in their solid state because of strong electrostatic forces between the ions.

5. Ionic reactions. The ionic compounds split up into oppositely charged ions when dissolved in water. The chemical reactions of ionic compounds are characteristic of the constituent ions and are known as **ionic reactions**. Such reactions occur almost instantaneously.

6. Non-directional character. The ionic bond is non-directional. In ionic-compounds, each ion is surrounded by oppositely charged ions uniformly distributed all around the ion and therefore, electrical field is non-directional. Thus, the ionic bond is non-directional.

SOLVED EXAMPLES

Example 3.

Give the Lewis structures and empirical formulae for the ionic compounds formed between the following pairs of elements :

(i) Ba, Cl (ii) Na, S (iii) Al, F (iv) Mg, N (v) Na, P

Solution: From the charges on the ions, the number of positive and negative ions in the compound can be found out. This gives the empirical formula (E.F.)

(*i*) $\dot{Ba}\cdot$, $:\dot{\underset{\cdot\cdot}{Cl}}:$ ⟶ Ba^{2+} , Cl^- (ions)

Lewis formula : $[Ba]^{2+}$ $2\,[:\dot{\underset{\cdot\cdot}{Cl}}:]^-$, or $BaCl_2$

(*ii*) $\dot{Na}$, $:\dot{\underset{\cdot\cdot}{S}}:$ ⟶ Na^+, S^{2-} (ions)

Lewis formula : $2[Na]^+$ $[:\dot{\underset{\cdot\cdot}{S}}:]^{2-}$, or Na_2S

(*iii*) $\dot{Al}\cdot$, $\cdot\dot{\underset{\cdot\cdot}{F}}:$ ⟶ Al^{3+} , F^- (ions)

Lewis formula : $[Al]^{3+}$ $3[:\dot{\underset{\cdot\cdot}{F}}:]^-$, or AlF_3

(*iv*) $\dot{Mg}$, $\cdot\dot{\underset{\cdot}{N}}\cdot$ ⟶ Mg^{2+} , N^{3-} (ions)

Lewis formula : $3[Mg]^{2+}$ $2[:\dot{\underset{\cdot}{N}}:]^{3-}$, or Mg_3N_2

(*v*) $\dot{Na}$, $\cdot\dot{\underset{\cdot\cdot}{P}}:$ ⟶ Na^+, $:\dot{\underset{\cdot\cdot}{P}}:^{3-}$ (ions)

Lewis formula : $3[Na]^+$ $[:\dot{\underset{\cdot\cdot}{P}}:]^{3-}$, or Na_3P

Example 4.

Use Lewis symbols to show electron transfer between the following atoms to form cations and anions : ***N.C.E.R.T.***

(i) K and S (ii) Ca and O (iii) Al and N

Solution:

(*i*) $\dot{K}$, $:\dot{\underset{\cdot\cdot}{S}}:$, $\dot{K}$ ⟶ K^+ $[:\dot{\underset{\cdot\cdot}{S}}:]^{2-}$ K^+ or K_2S

(*ii*) $\dot{Ca}\cdot$, $:\dot{\underset{\cdot\cdot}{O}}:$ ⟶ Ca^{2+} $[:\dot{\underset{\cdot\cdot}{O}}:]^{2-}$ or CaO

(*ii*) $\dot{Al}\cdot$, $\cdot\dot{\underset{\cdot}{N}}:$ ⟶ Al^{3+} $[:\dot{\underset{\cdot}{N}}:]^{3-}$ or AlN

Practice Problems

5. Draw the Lewis structures for the following ionic compounds :

(*i*) Li_2O (*ii*) $CaCl_2$ (*iii*) LiF

6. Draw the Lewis structures for K_2O and $MgCl_2$.

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COVALENT BOND

In 1919, Langmuir refined the Lewis postulations and introduced the term **covalent bond.** According to Lewis–Langmuir theory, atoms can combine by sharing of electrons between them. This type of bond is called covalent bond and each atom contributes equal number of electrons for sharing in order to acquire configuration of nearest noble gas. Thus,

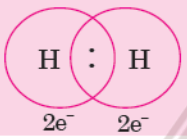
the bond formed by mutual sharing of electrons between the combining atoms of the same or different elements is called a **covalent bond.**

The compounds so formed are called **covalent compounds.**

Let us consider the formation of a hydrogen molecule from two hydrogen atoms. When two hydrogen atoms approach each other, the single electron of both the atoms forms a shared pair. The shared pair now belongs simultaneously to both the hydrogen atoms *i.e., it is contained by electron shells of both the atoms.* Each hydrogen atom can now be thought of as having noble gas configuration of helium ($1s^2$). This may be represented as :

$$H^{\bullet} + H^{\bullet} \longrightarrow \underset{\text{Sharing of electrons}}{H:H} \quad \text{or} \quad \underset{\text{Hydrogen molecule}}{H—H}$$

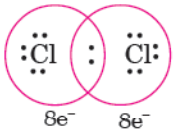
The sharing of electrons can also be shown by drawing a circle around each atom. This also helps us to count the electrons around any atom; the shared electron pair is thought of as belonging exclusively to that atom. For example, H_2 molecule is shown as



Similarly, two chlorine atoms combine with each other to form a molecule of chlorine. In this case, both the atoms have seven electrons in the outermost shell ([Ne] $3s^2\ 3p^5$) and have one electron less than argon configuration. Therefore, they contribute one electron each to form a shared pair between two atoms. In this process, both chlorine atoms attain the stable electronic configuration of noble gas (octet). This results in the formation of a covalent bond in Cl_2 molecule. This may be depicted as :

$$:\ddot{\underset{\cdot\cdot}{Cl}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow :\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{Cl}}: \quad \text{or}$$

Chlorine atoms — Chlorine molecule



However, a covalent bond is not only formed between similar atoms but it may also be formed between dissimilar atoms. For example, hydrogen and chlorine form a covalent bond between their atoms. In HCl, hydrogen atoms has only one electron and chlorine atom has seven electrons in its valence shell. Therefore, by mutual sharing of electron pair between a hydrogen atom and a chlorine atom, both the atoms acquire nearest noble gas configurations. Hydrogen atom acquires electronic configuration of helium whereas chlorine atom gets electronic configuration of argon.

$$H^{\bullet} + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow H:\ddot{\underset{\cdot\cdot}{Cl}}: \quad \text{or} \quad \underset{\text{Hydrogen chloride}}{H—Cl}$$

Lewis Structures and Covalent Bond

Conditions for writing the Lewis dot structures of molecules

The main conditions for writing the electron dot (or Lewis) structures of covalent molecules are :

(*i*) Each bond is formed as a result of sharing of an electron pair between the atoms.

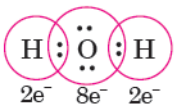
(*ii*) Each combining atom contributes one electron to the shared pair.

(*iii*) Both the combining atoms attain the stable outer shell noble gas configurations as a result of sharing of the electrons. In other words, octets of both the atoms get completed.

Electron dot (or Lewis) structures of covalent molecules are written in accordance with octet rule. According to this, all the atoms in a formula will have a total of eight electrons in the valence shell (shown) except the hydrogen atom. Hydrogen will have only two electrons because only two electrons complete its first shell as in helium. Thus, the elements of group 17 (containing seven valence electrons) such as Cl, would share one electron to attain stable octet; the elements of group 16 (containing six valence electrons) such as O and S would share two electrons; the elements of group 15 (containing five valence electrons) would share three electrons and so on. For example, oxygen (with six electrons in the valence shell) completes its octet by sharing its two electrons with two hydrogen atoms as shown below :

$$2H^{\bullet} + \cdot\ddot{\underset{\cdot\cdot}{O}}\cdot \longrightarrow H:\ddot{\underset{\cdot\cdot}{O}}:H$$

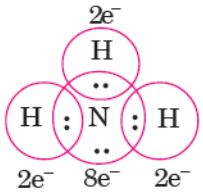
Water



Similarly, nitrogen has five electrons in its valence shell and shares with three hydrogen atoms to form ammonia.

$$3H^{\bullet} + \cdot\ddot{\underset{\cdot\cdot}{N}}\cdot \longrightarrow \underset{\cdot\cdot}{\overset{H}{\overset{|}{H:\ddot{N}:H}}}$$

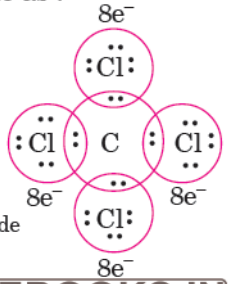
Ammonia



Similarly, carbon has four electrons in its valence shell and shares with four chlorine atoms to form carbon tetrachloride (CCl_4) molecule as :

$$4:\ddot{\underset{\cdot\cdot}{Cl}}\cdot + \cdot\dot{\underset{\cdot}{C}}\cdot \longrightarrow :\ddot{\underset{\cdot\cdot}{Cl}}:\underset{:\ddot{\underset{\cdot\cdot}{Cl}}:}{\overset{:\ddot{\underset{\cdot\cdot}{Cl}}:}{\overset{|}{\underset{|}{C}}}}:\ddot{\underset{\cdot\cdot}{Cl}}:$$

Carbon tetrachloride



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Lewis structures for molecules having multiple covalent bonds. If the normal valence of an atom is not satisfied by sharing single electron pair between atoms, the atoms may share more than one electron pair between them.

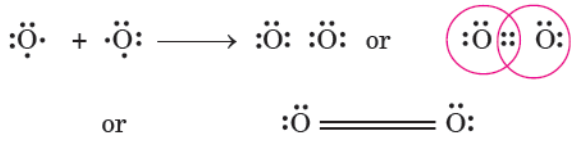
(*i*) *If two atoms share one electron pair,* bond is known as **single covalent bond** and is represented by one dash (—).

(*ii*) *If two atoms share two electron pairs,* bond is known as **double covalent bond** and is represented by two dashes (═).

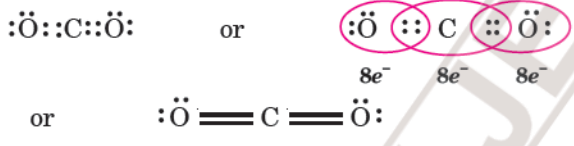
(*iii*) *If two atoms share three electron pairs,* bond is known as **triple covalent bond** and is represented by three dashes (≡).

Let us discuss some examples of molecules having double and triple bonds.

Oxygen molecule. In the formation of oxygen molecule, each oxygen atom has six electrons in the valence shell and requires two electrons to complete its octet. Therefore, both the atoms contribute two electrons each for sharing to form oxygen molecule. In this molecule, two electron pairs are shared and hence there is a double bond between the two oxygen atoms.

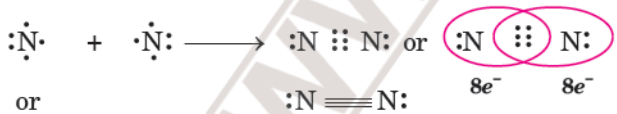


Carbon dioxide molecule. Carbon has four valence electrons and oxygen has six. To complete the octets, carbon shares two of its valence electrons with one oxygen atom and two with other oxygen atom.

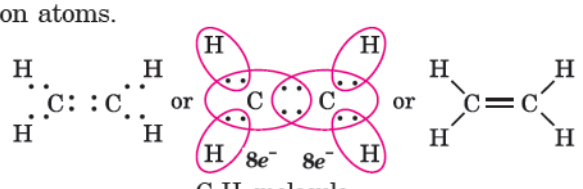


Thus, there are two double bonds in CO_2 molecule.

Nitrogen molecule. In the formation of a nitrogen molecule, each of the two nitrogen atoms having five valence electrons, provides three electrons to form three electron pairs for sharing. Thus, a triple bond is formed between the two nitrogen atoms.

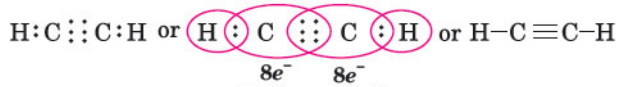


Ethylene molecule. In ethylene, each carbon atom shares two of its valence electrons with two hydrogen atoms and remaining two electrons with the second carbon atom. So, there is a double bond between carbon atoms.



C_2H_4 molecule

Acetylene molecule. In acetylene molecule, each carbon atom shares three of its valence electrons with other carbon atom forming a triple bond.



C_2H_2 molecule

Writing Lewis structures

The following steps are adopted for writing the Lewis dot structures or Lewis structures :

Step 1. Calculate the total number of electrons required for writing the structure by adding the valence electrons of the combining atoms. For example, in methane, CH_4 molecule, there are 8 valence electrons (4 from carbon and 4 from four H atoms).

Step 2. For anions, each negative charge means addition of an electron to the valence electrons and for cations, each positive charge means subtraction of one electron from the valence electrons.

Step 3. Knowing the chemical symbols of the combining atoms and guessing the skeletal structure of the compound, distribute the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds.

Step 4. In general, the least electronegative atom occupies the central position in the molecule. Hydrogen and fluorine generally occupy the terminal positions.

Step 5. After distributing the shared pairs of electrons for single bonds, the remaining electron pairs are used either for multiple bonds or they constitute lone pairs.

The basic requirement is that each bonded atom gets an octet of electrons.

Let us learn these steps by writing Lewis structures for some molecules or ions.

(*i*) **Lewis formula for carbon monoxide, CO**

Step 1. Counting the total number of valence electrons of carbon and oxygen atoms :

C $(2s^2 2p^2)$ + O $(2s^2 2p^4)$

4 + 6 = 10. *i.e.*, 4(C) + 6(O) =10

Step 2. The skeletal structure of CO is written as:

CO

Step 3. Drawing of a single bond between C and O and completing octet on O, the remaining two electrons are the lone pair on C.

:C: Ö: or :C—Ö:

Step 4. This does not complete octet on carbon and, hence, we have triple bond between C and O atom.

:C⋮⋮O: or :C ≡ O:

This satisfies octet rule condition for both atoms.

(*ii*) **Lewis formula for formic acid (HCOOH)**

Step 1. Counting the total number of valence electrons

Total number of valence electrons are:

C $(2s^2 2p^2)$ + 2H$(1s^1)$ + 2O $(2s^2 2p^4)$

$4 + 2 \times 1 + 2 \times 6 = 18$.

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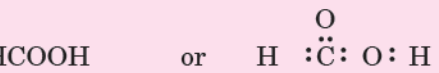
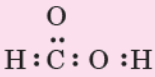
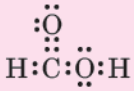
Step 2. The skeletal structure of formic acid suggested by molecular formula is :

HCOOH or 

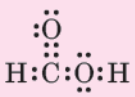
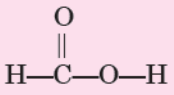
Step 3. Use four electron pairs to form single bond between neighbouring atoms



Step 4. Complete octet of each atom (except H) by adding two lone pairs on each oxygen atom and one oxygen gets double bond between C and O.



Hence the final Lewis structure is

 or 

(iii) **Lewis structure of nitrite, NO_2^- ion**

Step 1. Counting the total number of valence electrons of one nitrogen atom, two oxygen atoms and the additional one negative charge (equal to one electron).

Total number of valence electrons are :

$N(2s^2 2p^3) + 2O(2s^2 2p^4) + 1$ (–ve charge)

$5 + 2 \times 6 + 1 = 18$

Step 2. The skeletal structure of NO_2^- ion is written as :

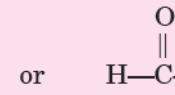
O N O

Step 3. Draw single bonds between nitrogen and each oxygen atom.

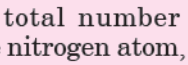
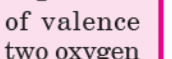
O : N : O

Step 4. Complete the octets of atoms.

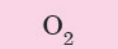
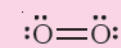
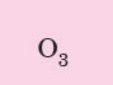
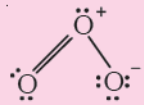
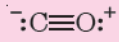
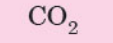
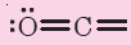
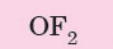
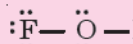
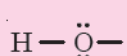
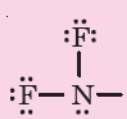
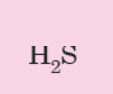
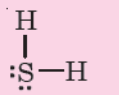
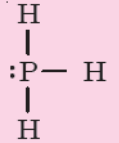
This structure does not complete octet on N if the remaining two electrons constitute a lone pair on it . Therefore, we have double bond between one N and one of the two O atoms.

 or

The Lewis structure is

 or 

Lewis dot representation of some molecules or ions are summarized below :

Molecule/ion	Lewis Representation		
O_2		or	
O_3		or	
CO		or	
CO_2		or	
OF_2		or	
H_2O_2		or	
NF_3		or	
H_2S		or	
PH_3		or	

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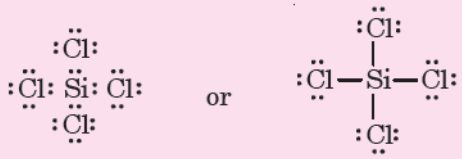
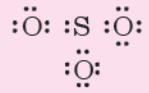
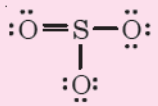
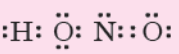
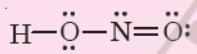
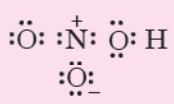
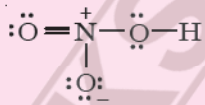
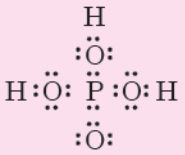
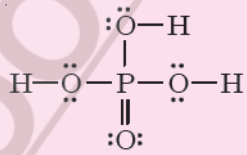
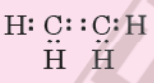
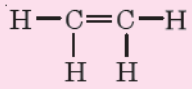
$SiCl_4$  or

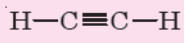
SO_3  or 

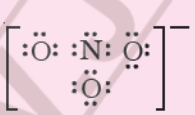
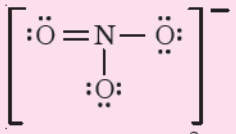
HNO_2 (Nitrous acid)  or 

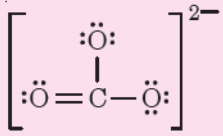
HNO_3 (Nitric acid)  or 

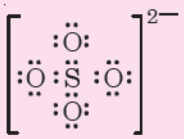
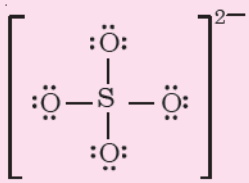
H_3PO_4 (Phosphoric acid)  or 

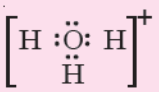
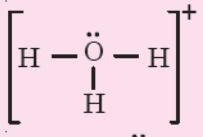
C_2H_4 (Ethylene)  or 

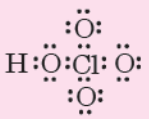
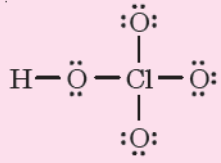
C_2H_2 (Acetylene) or 

NO_3^-  or 

CO_3^{2-} or 

SO_4^{2-}  or 

H_3O^+  or 

$HClO_4$ (Perchloric acid)  or 

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Formal charge

In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is possible, however, to assign a formal charge on each atom. The ***formal charge of an atom in a polyatomic ion or molecule*** is defined as

the difference between the number of valence electrons in an isolated (or free) atom and the number of electrons assigned to that atom in a Lewis structure.

It may be expressed as :

Formal charge on an atom in a Lewis structure =

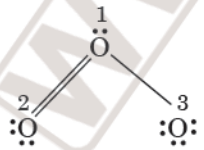
$$\left(\begin{array}{c}\text{total number of}\\ \text{valence electrons}\\ \text{in free atom}\end{array}\right) - \left(\begin{array}{c}\text{total number of}\\ \text{nonbonding}\\ \text{(lone pair) electrons}\end{array}\right) - \frac{1}{2}\left(\begin{array}{c}\text{total number of}\\ \text{bonding}\\ \text{(shared) electrons}\end{array}\right)$$

or $$FC = V - L - \frac{1}{2}S$$

where FC = Formal charge on an atom
V = Total number of valence electrons in the free atom
L = Total number of electrons present as non-bonding (lone pair)
S = Total number of bonding (shared) electrons.

The counting is based on the assumption that each atom owns one electron of each bonding pair and both the electrons of a lone pair. We can count the number of electrons assigned to an atom on this assumption and then compare the number with the number of electrons in the free atom. If the atom has more electrons in the molecule than in the free or neutral atom, then the atom has a negative formal charge. On the other hand, if the atom has less electrons in the molecule than in the free or neutral atom, then it has a positive formal charge.

Let us consider ozone molecule. The ozone molecule may be represented as :



The central O atom marked 1 has 6 valence electrons, one lone pair (2 electrons) and three bonds (or 6 bonding electrons). Therefore, its formal charge is

$$FC \text{ on O (1)} = 6 - 2 - \frac{1}{2} \times 6 = +1$$

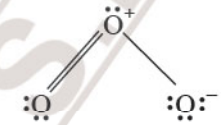
The end O atom marked 2 has 6 valence electrons, two lone pairs (4 electrons) and two bonds (4 bonding electrons). Therefore, its formal charge is

$$FC \text{ on O(2)} = 6 - 4 - \frac{1}{2}(4) = 0$$

The end O atom marked 3 has 6 valence electrons, three lone pairs (6 electrons) and one bond (2 bonding electrons). Therefore, its formal charge is

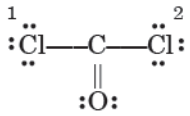
$$FC \text{ on O (3)} = 6 - 6 - \frac{1}{2}(2) = -1$$

Therefore, the formal charges on the oxygen atoms in the Lewis structures of ozone molecule are written as :



It may be noted that formal charges do not indicate real charge separation within the molecules. *These only help in keeping track of the valence electrons in the molecule.* **The formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given molecule or ion. In general, the lowest energy structure is the one, which has lowest formal charges on the atoms.**

Let us consider another example of phosgene ($COCl_2$) which is a poisonous gas.



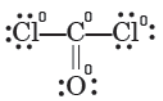
Cl (1)
Valence electrons = 7
Lone pair electrons = 6
Bond pair electrons = 2
$\therefore FC = 7 - 6 - \frac{1}{2}(2)$
$= 0$

Cl (2)
Valence electrons = 7
Lone pair electrons = 6
Bond pair electrons = 2
$\therefore FC = 7 - 6 - \frac{1}{2}(2)$
$= 0$

O atom
Valence electrons = 6
Lone pair electrons = 4
Bond pair electrons = 4
$\therefore FC = 6 - 4 - \frac{1}{2}(4)$
$= 0$

C atom
Valence electrons = 4
Lone pair electrons = 0
Bond pair electrons = 8
$\therefore FC = 4 - 0 - \frac{1}{2}(8)$
$= 0$

Thus,



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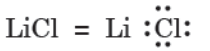
Exceptions to the Octet Rule.

Although octet rule is useful in a large number of cases, it has many exceptions also. Some important exceptions of octet rule are given below :

1. Hydrogen molecule. Hydrogen has one electron in its first energy shell (n = 1). It needs only one more electron to fill this shell, because the first shell cannot have more than two electrons. This configuration ($1s^2$) is similar to that of noble gas helium and is stable. In this case, therefore, octet is not needed to achieve a stable configuration.

2. Incomplete octet of the central atom. The octet rule cannot explain the formation of certain molecules of lithium, beryllium, boron, aluminium, etc. (LiCl, BeH_2, $BeCl_2$, BH_3, BF_3) in which the central atom has less than eight electrons in the valence shell. These are electron deficient compounds as shown below :

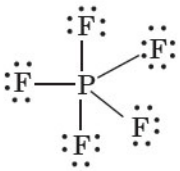


2 electrons around central Li-atom

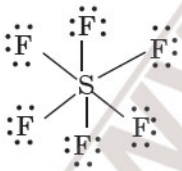
4 electrons around central Be-atom

6 electrons around central B-atom

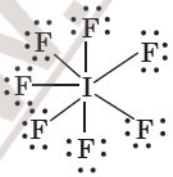
3. Expanded octet of the central atom. There are many stable molecules which have more than eight electrons in their valence shells. For example, PF_5 has ten; SF_6 has twelve and IF_7 has fourteen electrons around the central atoms, P, S and I respectively, as shown below :



(10 electrons around P)

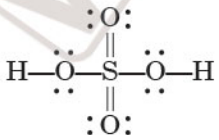


(12 electrons around S)



(14 electrons around I)

Similarly, in sulphuric acid, there are twelve electrons around the sulphur atoms.



12 electrons around S atom

These compounds in which the atom has more than 8 electrons around it are called **hypervalent compounds.**

However, it may be noted that sulphur also forms many compounds in which the octet rule is obeyed.

For example, in sulphur dichloride, the S atom has an octet of electrons around it.

4. Odd electron molecules. There are certain molecules which have odd number of electrons, like nitric oxide, NO and nitrogen dioxide, NO_2. In these cases, octet rule is not satisfied for all the atoms.

Nitric oxide Nitrogen dioxide

The other examples of molecules having odd number of electrons are ozone (O_3), superoxide ion (O_2^-) etc.

Other drawbacks of the octet rule

5. It may be noted that the octet rule is based upon the chemical inertness of noble gases. However, it has been found that some noble gases (especially xenon and krypton) also combine with oxygen and fluorine to form a large number of compounds such as XeF_2, KrF_2, $XeOF_2$, $XeOF_4$, XeF_6, etc.

6. This theory does not account for the shape of the molecules.

7. It cannot explain the relative stability of the molecule in terms of the energy.

GENERAL PROPERTIES OF COVALENT COMPOUNDS

The main characteristic properties of covalent compounds are :

1. State of existence. The covalent compounds do not exist as ions but they exist as molecules. There are weak intermolecular forces between the molecules and hence, they exist as liquids or gases at room temperature. However, a few compounds also exist in the solid state *e.g.*, urea, sugar, etc.

2. Low melting and boiling points. The melting and boiling points of covalent compounds are generally low. This is because of the fact that the forces between the molecules are weak and are easily overcome at low temperatures.

3. Solubility. Covalent compounds are generally insoluble or less soluble in water and other polar solvents. However, these are soluble in non-polar solvents such as benzene, carbon-tetrachloride, etc.

4. Non-conductors. Since covalent compounds do not give ions in solution, these are poor conductors of electricity in the fused or dissolved state.

5. Molecular reactions. The reactions between covalent compounds occur between their molecules. These involve the breaking of covalent bonds in reacting molecules and forming new covalent bonds to give molecules of the products. These **reactions are quite slow** because energy is required to break covalent bonds.

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6. Directional character of bond. Since the covalent bond is localised in between the nuclei of atoms, it is directional in nature.

SOLVED EXAMPLES

Example 5.

Draw Lewis structures for the following molecules and identify the atoms in each of the following which do not obey octet rule :

H_2S SF_2 BF_3 SO_2 PCl_3

Solution: The Lewis structures for the molecules may be written on the basis of number of electrons in the valence shell of the central atom, and shared electron pairs with the other atoms as shown below :

(*i*) $H_2S = 2H + \cdot\ddot{S}: \longrightarrow H:\underset{H}{\ddot{S}}:$

Two H-atoms do not obey octet rule.

(*ii*) $SF_2 = :\ddot{S}\cdot + 2\ \cdot\ddot{F}: \longrightarrow :\ddot{F}\ :\ddot{S}:\ \ddot{F}:$

All atoms obey octet rule.

(*iii*) $BF_3 = \cdot\dot{B}\cdot + 3\ \cdot\ddot{F}: \longrightarrow :\underset{:\ddot{F}:}{\ddot{F}}:\ B\ :\ddot{F}:$

Boron does not obey octet rule.

(*iv*) $SO_2 = \cdot\ddot{S}: + 2\ \cdot\ddot{O}: \longrightarrow :\ddot{O}::S::\ddot{O}:$

S-atom does not obey octet rule.

(*v*) $PCl_3 = \cdot\ddot{P}\cdot + 3\ \cdot\ddot{Cl}: \longrightarrow :\ddot{Cl}\ :\ddot{P}:\ \ddot{Cl}:$ with $:\ddot{Cl}:$ below

All atoms obey octet rule.

Example 6.

Calculate the formal charges on the atoms in

(i) Nitrite ion

(ii) Carbonate ion

Solution:

(*i*) Lewis structure of nitrite ion is

$:\ddot{O} = \ddot{N} - \ddot{O}:^-$

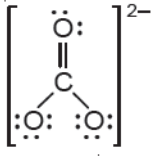
FC on N atom $= V - L - \frac{1}{2}S$

$= 5 - 2 - \frac{1}{2}(6) = 0$

FC on double bonded O atom $= 6 - 4 - \frac{1}{2}(4) = 0$

FC on single bonded O atom $= 6 - 6 - \frac{1}{2}(2) = -1$

(*ii*) Lewis structure of carbonate ion is



FC on C atom $= 4 - 0 - \frac{1}{2}(8) = 0$

FC on double bonded O atom

$= 6 - 4 - \frac{1}{2}(4) = 0$

FC on single bonded O atom

$= 6 - 6 - \frac{1}{2}(2) = -1$

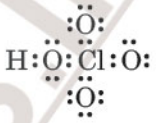
Example 7.

Calculate the formal charge on

(i) Cl in $HClO_4$ (ii) S in HSO_4^-

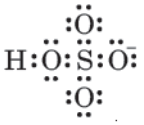
Solution:

(*i*) Lewis structure of $HClO_4$ is



FC on Cl atom $= 7 - 0 - \frac{1}{2}(8) = +3$

(*ii*) Lewis structure of HSO_4^- is



F.C. on S atom $= 6 - 0 - \frac{1}{2}(8)$

$= 6 - 4 = +2$

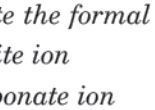
Practice Problems

7. Draw Lewis dot structures for the following molecules :

(*a*) CCl_4 (*b*) F_2O (*c*) PF_3 (*d*) F_2

(*e*) ClF_3 (*f*) NCl_3 (*g*) HONO

8. The skeleton structure for acetaldehyde (CH_3CHO) is :



Draw its Lewis structure.

9. Draw Lewis structures for the following molecules and ions :

AlI_3, $SiCl_4$, CO_3^{2-}, HCOOH

10. Write the Lewis structures for

(*i*) CO (*ii*) NH_2CONH_2 (urea)

(*iii*) H_2CCH_2 (ethene) (*iv*) HNO_3

CO-ORDINATE COVALENT BOND

So far, we have considered that in single covalent bonds each atom contributes one electron. The shared pair of electrons is provided to a bond by one atom only and the other atom merely participates in sharing. Perkin (in 1921), suggested another covalent type bond in which *both the electrons in the shared pair come from one atom. This is called* a **coordinate covalent bond.** Such type of bond is formed between atoms (or ions), one of which is deficient in at least two electrons while the other atom has already acquired a stable noble gas configuration (or octet). The atom which contributes the electrons is called the **donor** while

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the other which only shares the electron pair is known as **acceptor.** *This bond is usually represented by an arrow (⟶) pointing from donor to the acceptor atom.* This type of bond has also been named as **dative bond, donor-acceptor bond, semi-polar bond or co-ionic bond.** For example, a hydrogen ion combines with ammonia molecule by a coordinate covalent bond to form ammonium ion (NH_4^+):

Donor Acceptor

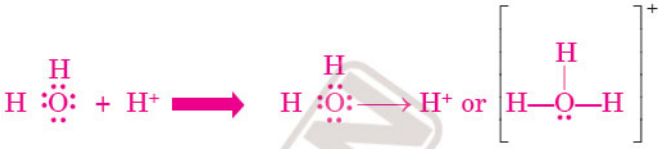
It may be remembered that in the modern terminology, there is no distinction between a covalent bond and a coordinate bond. Once the coordinate bond is formed, it cannot be distinguished from the normal covalent bond.

A few examples of this type of bond are given below :

(i) **Ozone molecule (O_3).** A molecule of oxygen contains two oxygen atoms joined by double covalent bond so that octet of each of the two atoms is complete. Now, if an atom of oxygen having six electrons comes close to oxygen molecule, the new atom may share a lone pair of electrons of one of the oxygen atoms of the oxygen molecule. This results in the formation of a co-ordinate bond as shown below :

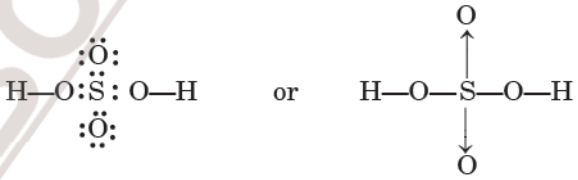
Oxygen molecule Oxygen atom

(ii) **Hydronium ion (H_3O^+).** Water, (H_2O) has two lone pairs of electrons on oxygen atom while H^+ ion has empty 1*s*-shell. Thus, oxygen atom can easily donate two electrons to H^+ ion.



(iii) **Ammonia (NH_3) and boron trifluoride (BF_3).** These molecules also combine through a co-ordinate bond as shown below :

(iv) **Sulphuric acid, (H_2SO_4).** Sulphuric acid has also two co-ordinate bonds in its molecule. As given below, the bonds between the sulphur atom and the oxygen atom of two—OH groups are the normal single bonds, whereas, the bonds between sulphur atom and the other two oxygen atoms are co-ordinate bonds.



add on Conceptual Questions 1

CONCEPTUAL QA

Q. 1. Out of MgO and NaCl, which has higher lattice energy and why ?

Ans. MgO has higher lattice energy because both the ions carry two unit charges whereas in NaCl, each ion carries one unit charge.

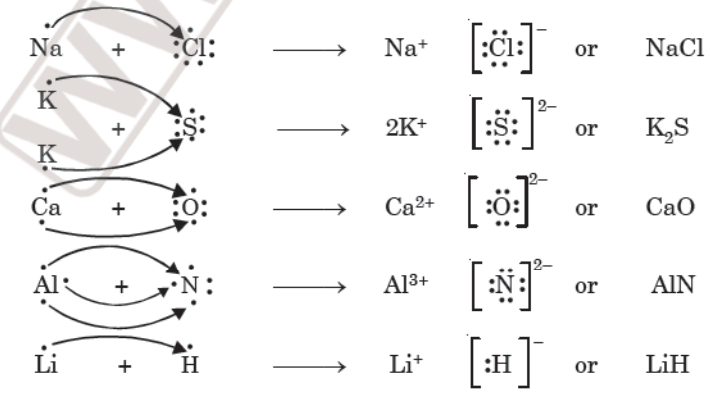
Q. 2. Why is NaCl a bad conductor of electricity in the solid state ?

Ans. In the solid state, Na^+ and Cl^- ions are strongly held together and are not free to move.

Q. 3. Use Lewis dot symbols to show electron transfer between the following atoms to form cations and anions :

(a) Na and Cl (b) K and S (c) Ca and O (d) Al and N (e) Li and H

Ans.



Q. 4. Write Lewis dot symbols for the following elements :
Mg, Na, B, O, N, Br

N.C.E.R.T.

Ans.

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Q. 5. Write Lewis symbol for the following stoms and ions :
S and S^{2-}, Al and Al^{3+}, H and H^- *N.C.E.R.T.*

Ans. $:\dot{\underset{\cdot}{\overset{\cdot}{S}}}\cdot$ and $[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:]^{2-}$ $\cdot\dot{Al}\cdot$ and Al^{3+} $\dot{H}$ and $[\ddot{H}]^-$

Q. 6. Write Lewis dot symbols for O and O^{2-}

Ans. $\cdot\dot{\underset{\cdot}{\overset{\cdot}{O}}}:$ and $[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:]^{2-}$

Q. 7. Which of the two is more hard : MgO or CaO ? The internuclear distances of MgO and CaO are 2.05 and 2.40 Å respectively.

Ans. MgO because MgO has less interionic distance than CaO (both have same charges) and, therefore, electrostatic force of attraction is more in MgO.

CONCEPTUAL QA

Q. 8. Why does NaCl give a white precipitate with $AgNO_3$ solution but CCl_4 does not ?

Ans. NaCl is an ionic compound and gives Cl^- ions in the solution. These Cl^- ions react with Ag^+ ions given by $AgNO_3$ to form a white precipitate of AgCl.

Cl^- (from NaCl) + Ag^+ (from $AgNO_3$) $\longrightarrow$ AgCl
White ppt.

However, CCl_4 is a covalent compound and does not give Cl^- ions to react with Ag^+ (or $AgNO_3$).

Q. 9. Calculate the formal charge on each atom in

$:\ddot{\underset{\cdot\cdot}{O}}-\ddot{\underset{\cdot\cdot}{S}}=\ddot{\underset{\cdot\cdot}{O}}:$

Ans. $:\ddot{\underset{\cdot\cdot}{O}}-\ddot{\underset{\cdot\cdot}{S}}=\ddot{\underset{\cdot\cdot}{O}}:$

Formal charge on atom
$= \text{No. of valence electrons} - \text{No. of non-bonding electrons} - \frac{1}{2}\text{ No. of bonding electrons}$

FC on S atom $= 6 - 2 - \frac{1}{2}(6) = +1$
FC on double bonded O atom $= 6 - 4 - \frac{1}{2}(4) = 0$
FC on single bonded O atom $= 6 - 6 - \frac{1}{2}(2) = -1$

So, we may write :

$:\overset{-1}{\ddot{\underset{\cdot\cdot}{O}}}-\overset{+1}{\ddot{\underset{\cdot\cdot}{S}}}=\overset{0}{\ddot{\underset{\cdot\cdot}{O}}}:$

Q. 10. Identify the compound/compounds in which S does not obey octet rule:
SO_2, SO_3, SF_4, SF_6, SF_2, H_2S

Ans. SF_4, SF_6

Q. 11. How is lattice enthalpy related to stability of an ionic compound?

Ans. Larger the lattice enthalpy of an ionic compound larger is its stability.

Q. 12. Give one example of a molecule not obeying octet rule.

Ans. PF_5

BOND PARAMETERS

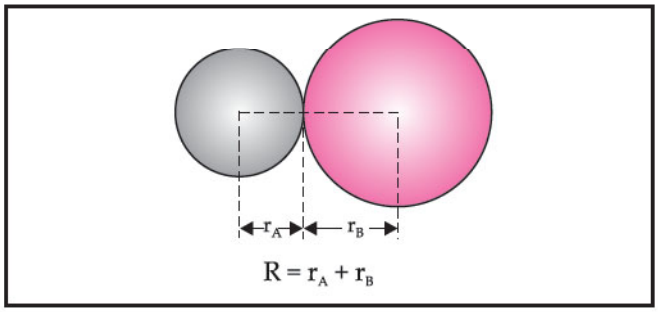
Covalent bonds are characterised by certain parameters such as bond length, bond angle and bond energy.

1. Bond length

Bond length is defined as

the equilibrium distance between the centres of the nuclei of two bonded atoms in a molecule.

Therefore, *it represents equilibrium internuclear separation distance of the bonded atoms in a molecule.*



It is measured by spectroscopic, X-ray diffraction and electron diffraction techniques. Each atom of the bonded pair contributes to bond length. In the case of a covalent bond, the contribution from each atom is called the **covalent radius** of that atom. The bond length in a covalent molecule AB may be expressed as

$$R = r_A + r_B$$

where R is the bond length and r_A and r_B are the covalent radii of atoms A and B respectively. Thus, the bond length is approximately the sum of the covalent radii of two atoms. For example, the O — H bond length in ethanol is the sum of the covalent radii of H and O, *i.e.* 37 + 74 = 111 pm. It is usually expressed in Angstrom units (Å) or picometers (pm).

1 Å = 10^{-10} m and 1 pm = 10^{-12} m.

The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an atom in a bonded situation. As already studied in Unit 3, covalent radius is half of the distance between two similar atoms joined by a covalent bond in the same molecule. On the other hand, the **van der Waals radius** represents the overall size of the atom which includes its valence shell

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in a nonbonded situation. ***Van der Waals radius*** *is* ***one half of the distance between two similar adjacent atoms belonging to two nearest neighbouring molecules of the same substance in the solid state.*** Covalent and van der Waals radii of chlorine are shown in Fig. 2.

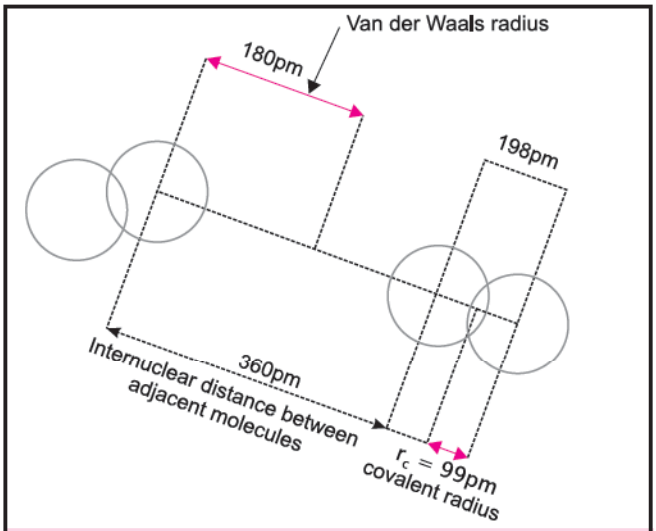

Fig. 2. Covalent and van der Waals radii of chlorine.

It is clear from Fig. 2., the internuclear distance between two atoms of the same molecule is 198 pm so that

$$r_{\text{covalent}} = \frac{198}{2} = 99 \text{ pm}.$$

The internuclear distance between two non-bonded nearest neighbouring atoms is 360 pm so that

$$r_{\text{van der Waals}} = \frac{360}{2} = 180 \text{ pm}$$

The van der Waals radii are always larger than covalent radii.

The average bond lengths for some single, double and triple bonds are given in Table 3 and the bond lengths for some common molecules are given in Table 4.

Table 3. Average bond lengths of some common bonds (single, double and triple) (pm).

Bond	Bond Length
O—H	96
C—H	107
C—N	143
C—C	154
Si—Si	234
Ge—Ge	244
N—O	136
C = C	134
C = N	138
N=O	122
C ≡ C	120
C ≡ N	116

Table 4. Bond length in some common molecules (pm).

Molecule	Bond Length
H_2(H—H)	74
F_2(F—F)	144
Cl_2(Cl—Cl)	198
Br_2(Br —Br)	228
I_2(I—I)	267
HF(H—F)	92
HCl(H—Cl)	127
HBr(H—Br)	141
HI(H—I)	160
N_2(N ≡ N)	109
O_2(O = O)	121

Factors affecting bond length

Bond length depends upon the following factors :

(*i*) Bond multiplicity

Bond length decreases with increase in bond multiplicity. Thus, C ≡ C bond length is shorter than C = C bond which in turn is shorter than C—C bond,

i.e., C ≡ C < C = C < C — C.

Similarly,

N ≡ N < N = N < N — N and O = O < O — O.

(*ii*) Size of the atom

The bond length increases with increase in the size of the atoms. It is also clear from the table that the bond lengths for a given family increase with increase in atomic number. For example,

C — C < Si — Si < Ge — Ge

This is expected because with the increase in size of the atom, the distance of the valence electrons from the nucleus increases successively with the addition of a new shell. Consequently, the distance between the bonding nuclei (bond length) increases.

2. Bond angle

Bond angle may be defined as

the average angle between the orbitals containing bonding electron pairs around the central atom in a molecule.

It is expressed in degree/minute/second. Bond angle gives an idea about the distribution of orbitals around the central atom in a molecule and therefore, determines the shape of a molecule. For example, the H—C—H bond angle in methane is 109.5°, the H—O—H bond angle in H_2O is 104.5° and H—N—H bond angle in ammonia is 107°.

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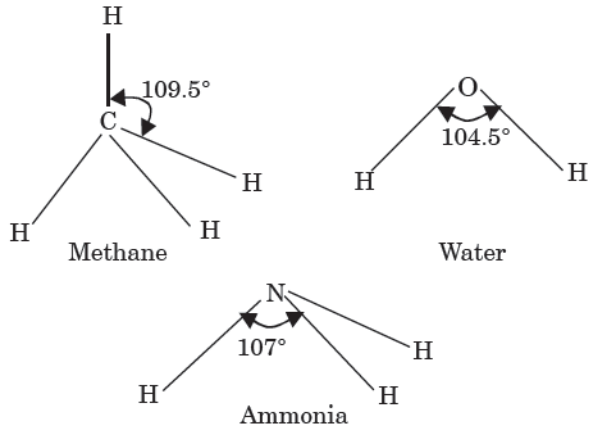

3. Bond enthalpy

We have learnt that when a bond is formed between the atoms, energy is released. This means that the bonded atoms have lesser energy than the separated individual atoms. Obviously, the same amount of energy will be needed to break the bond. This is called **bond dissociation enthalpy** and is measure of *bond strength*. **Bond dissociation enthalpy** may be defined as

the amount of energy required to break one mole of bonds of a particular type between the atoms in the gaseous state.

It is generally expressed in terms of kJ mol^{-1}. For example, the bond dissociation enthalpy of H—H bond in hydrogen molecules is 435.8 kJ mol^{-1}.

$$H_2(g) \longrightarrow H(g) + H(g) \quad \Delta_a H^\circ = 435.8 \text{ kJ mol}^{-1}$$

Similarly, the bond dissociation enthalpy of Cl—Cl in Cl_2 is 242.5 kJ mol^{-1}, I—I in I_2 is 151 kJ mol^{-1} and H—I in HI is 298.3 kJ mol^{-1}, etc. Similarly, for molecules containing double bond (O_2) and triple bond (N_2), bond dissociation enthalpies are :

$$O_2\ [O = O]\ (g) \longrightarrow O(g) + O(g)\ \Delta_a H^\circ = 498.0 \text{ kJ mol}^{-1}$$

$$N_2\ [N \equiv N]\ (g) \longrightarrow N(g) + N(g)\ \Delta_a H^\circ = 946.0 \text{ kJ mol}^{-1}$$

It may be noted that larger the bond dissociation enthalpy, stronger will be the bond in the molecule. The bond dissociation enthalpy of some simple bonds are given in Table 5.

Table 5. Bond dissociation enthalpy of some common bonds.

Bond	Bond dissociation enthalpy (kJ mol^{-1})
H—H	435.8
H—Cl	431.7
H—Br	366.1
H—I	298.3
F—F	158.1
Cl—Cl	243.5
Br—Br	192.8
I—I	151.0
N—H	389.2
O—H	464
O=O	498
C—H	414
C—C	433
C=C	619
C≡C	836
N≡N	946.0

Bond dissociation enthalpy depends upon two factors :

(*i*) **Size of the bonded atoms :** The smaller the size of the bonded atoms, the stronger is the bond. consequently, larger is the value of bond dissociation enthalpy. For example, the bond dissociation enthalpy of H—H bond (435.8 kJ mol^{-1}) is larger than the bond dissociation enthalpy of Cl—Cl bond (243.5 kJ mol^{-1}).

(*ii*) **Bond length :** Shorter the bond length, larger is the value of bond enthalpy. For example, C—C bond length (154 pm) is larger than C = C bond length (134 pm). Consequently, the bond dissociation enthalpy of C—C bond (433 kJ mol^{-1}) is smaller than that of C = C bond (619 kJ mol^{-1}).

Average bond enthalpy : Bond dissociation enthalpy of polyatomic molecules

In the case of polyatomic molecules (which contain more than one bond of the same type), the average of the bond enthalpies of the bonds are taken. The average of the bond dissociation enthalpies is called **average bond enthalpy** or simply as **bond enthalpy.** For example, in the case of water molecule, the enthalpy needed to break the two O–H bonds is not the same.

$$H_2O(g) \longrightarrow H(g) + OH(g) \quad \Delta_a H_1^\circ = 502 \text{ kJ mol}^{-1}$$

$$OH(g) \longrightarrow H(g) + O(g) \quad \Delta_a H_2^\circ = 427 \text{ kJ mol}^{-1}$$

The difference in the $\Delta_a H^\circ$ values suggests that the second O–H bond undergoes some change because of the changed chemical environment. This is the reason for some difference in energy of same O–H bond in different molecules such as CH_3OH (methanol), C_2H_5OH (ethanol), water, etc. Therefore for polyatomic molecules, mean or average bond enthalpy is used. It is obtained as the average of the different bond dissociation enthalpies in a molecule. For example, for water,

$$\text{Average bond enthalpy} = \frac{502 + 427}{2} = 464.5 \text{ kJ mol}^{-1}$$

Thus bond enthalpy is the average enthalpy required to break bonds of a given type in one mole of the gaseous molecules. Obviously, for diatomic molecules, the bond dissociation enthalpy is same as bond enthalpy.

4. Bond order

The bond order is defined as *the number of bonds between two atoms in a molecule.* For example, bond order in H_2 (with a single shared electron pair) is one, in O_2 (with two shared electron pairs) is two and in N_2 (with three shared electron pairs) is three.

H : H	Bond order = 1
O :: O	Bond order = 2
N ⁝ N	Bond order = 3
C ⁝ O	Bond order = 3

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It may be noted that **isoelectronic species** (molecules and ions) have same bond order. For example,

F_2, O_2^{2-} (18 electrons) have bond order 1

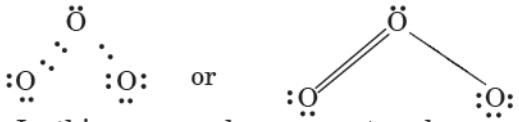
N_2, CO and NO^+ (14 electrons) have bond order = 3

It may be remembered that in general,

- **With increase in bond order, bond enthalpy increases and bond length decreases.**

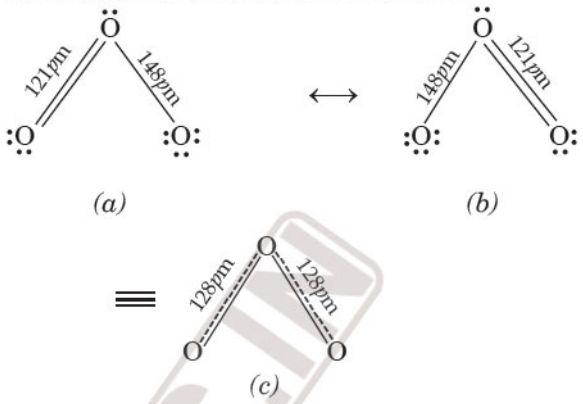
RESONANCE

The phenomenon of resonance was put forward by Heisenberg to explain the properties of certain molecules. It is often observed that a single Lewis structure is not adequate for the representation of a molecule in agreement with its experimentally determined parameters. To illustrate this consider a molecule of ozone (O_3). Its structure can be written as:



In this case, each oxygen atom has an octet of electrons. According to this structure, there is one single bond (O – O) and one double bond (O = O) in the molecule. The normal O–O and O=O bond lengths are 148 pm and 121 pm respectively. According to the above structure we would expect the two bond lengths in ozone molecule to be unequal. However, experimentally it is observed that both the bond lengths are equal (128 pm) and the bonds are intermediate between single and double bonds. This means that the above Lewis structure does not account for the observed experimental facts. To solve the problem, an alternative structure may be drawn as :

In this case, the double bond and the single bond are interchanged. But none of these two structures explains the observed facts. It is proposed that the actual structure is in between the two structures. In such a case, we say that the actual structure is a resonance hybrid of these two structures. The individual structures are called **resonance structures** or **contributing structures**. These are represented by drawing double headed arrows between these structures as shown below :



Thus, **resonance** may be summed up as :

when a molecule cannot be represented by a single structure but its characteristic properties can be described by two or more than two structures, then the actual structure is said to be a resonance hybrid of these structures.

For example, ozone molecule may be represented as a resonance hybrid of above two structures (*a*) and (*b*). For simplicity, ozone may be represented by structure (*c*) which shows the resonance hybrid having equal bonds between single and double.

Conditions for Writing Resonance Structures

The following are essential conditions for writing resonating structures :

1. The contributing structures should have same atomic positions.
2. The contributing structures should have same number of unpaired electrons.
3. The contributing structures should have nearly same energy.
4. The structures should be so written that negative charge is present on an electronegative atom and positive charge is present on an electropositive atom.
5. In contributing structures, the like charges should not reside on adjacent atoms.

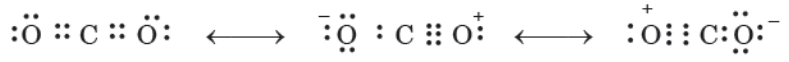
The contributing structures should not differ much in energy. This is an important condition. The individual structures of similar energy contribute equally to the resonance hybrid.

Let us discuss some other molecules :

(i) **Carbon dioxide molecule.** The simple structure of carbon dioxide molecule is

Therefore, we expect a double bond between carbon and oxygen atoms. The experimentally determined carbon to oxygen bond length in CO_2 molecule is 115 pm. The normal C = O bond length is 122 pm and C ≡ O bond length is 110 pm. This suggests that carbon-oxygen bond in CO_2 molecule is between double and triple bond.

Obviously, a single structure cannot depict the true structure of the molecule and it becomes necessary to write more than one Lewis structures. Therefore, the structure of CO_2 is best described as a resonance hybrid of the following three canonical forms :



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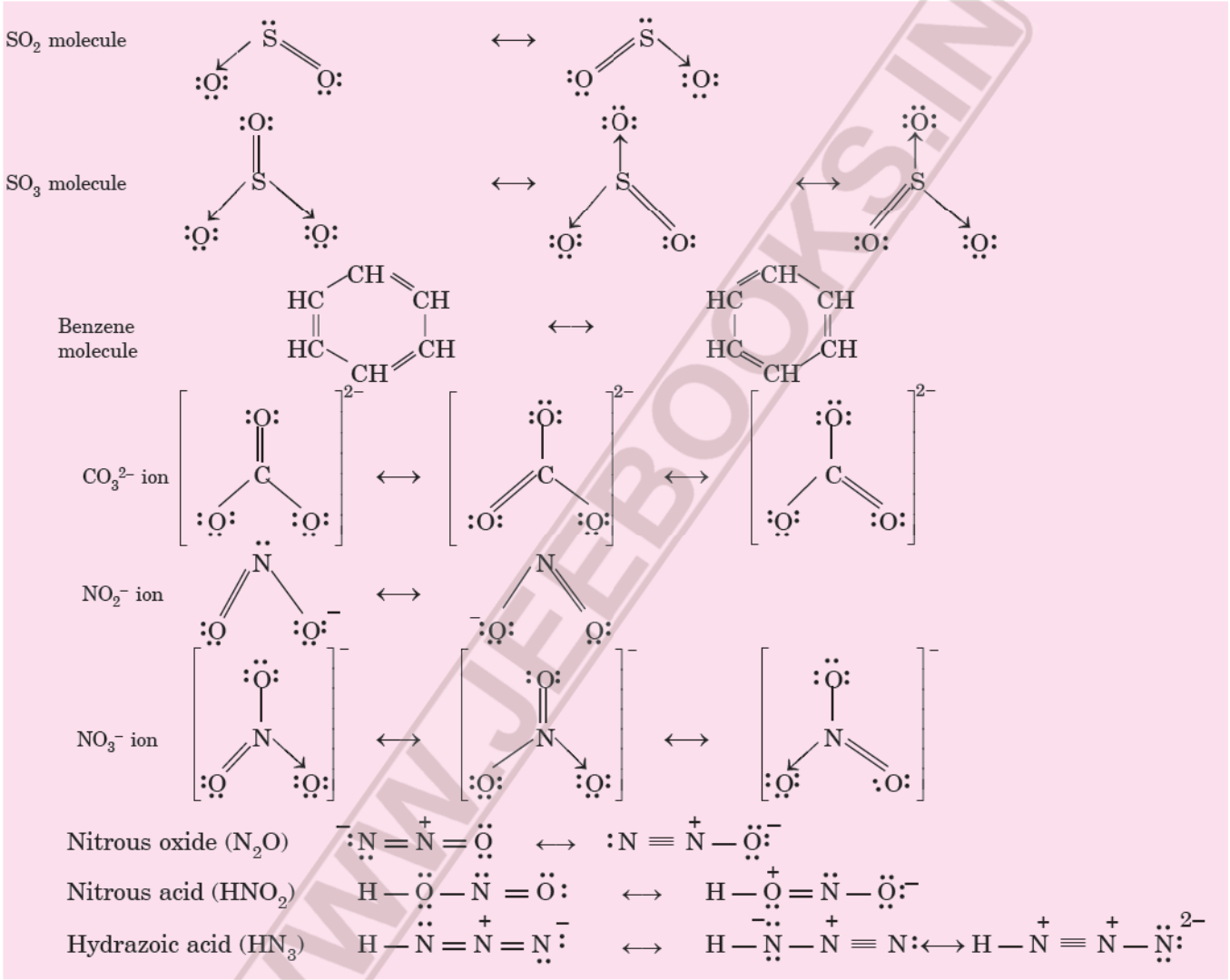
(*ii*) **Carbon monoxide molecule, CO.** The simple structure of carbon monoxide may be written as :

:C :: O:

Therefore, we expect a double bond in carbon and oxygen atoms. However, carbon-oxygen bond length has been experimentally determined to be 113 pm. This lies between normal C = O (122 pm) and C ≡ O (1.10 pm). Therefore, carbon monoxide has been proposed to be resonance hybrid of the following structures :

:C::O: ⟷ :C⁺:O:⁻ ⟷ :C⁻⋮⋮O⁺:

The resonance structures of a few more molecules and ions are given ahead.



Thus, we may conclude

- Resonance averages the bond characteristics of a molecule as a whole.
- Resonance stabilizes the molecule because the energy of the resonance hybrid is less than the energy of any single canonical structure.

Resonance energy. It is the difference between the actual bond energy of the molecule and that of the most stable of the resonating structures (having least energy). Thus,

Resonance energy =
Actual bond energy – Energy of the most stable of resonating structures.

For example, the resonance energy of carbon dioxide is 138 kJ mol^{-1}. This means that the actual molecule of CO_2 is about 138 kJ more stable than the most stable structure among the contributing structures. This can be easily illustrated as given below :

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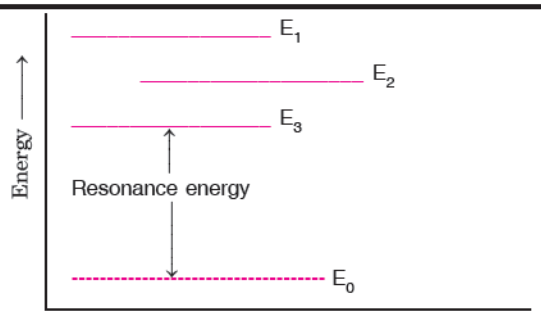


Fig. 3. Concept of resonance energy. Energies E_1, E_2 and E_3 are for three structures and E_0 is the experimentally determined bond energy.

Suppose E_1, E_2 and E_3 are the energies of three resonating structures for a molecule. Their energies are shown in Fig. 3. It is evident that among these, E_3 has the lowest energy (most stable contributing structure). If E_0 is the actual energy of the molecule (experimentally determined), then resonance energy is $E_3 - E_0$.

Characteristics of Resonance

1. The contributing structures do not have real existence. These are only imaginary proposed to explain the properties of the molecule. Only the resonance hybrid has the real existence.
2. Because of resonance, the bond lengths in a resonating structures become equal. For example, both the O—O bond lengths in O_3 are equal. All the C–C bonds in benzene are equal.
3. The resonance hybrid has lower energy and thus greater stability than any of the contributing structures.
4. Greater is the resonance and resonance energy, greater is the stability of the molecule.
5. Concept of resonance is a theoretical concept.

Calculation of Bond Order for Molecules Showing Resonance

In case of molecules or ions showing resonance, the contribution of each structure should be counted towards bond order. The bond order may be calculated as:

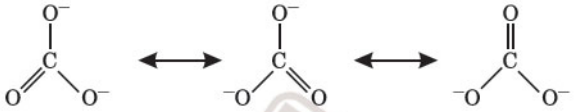
$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms in all the structures}}{\text{Total number of resonating structures}}$$

Any two bonded atoms may be selected and a double bond is counted as 2 bonds and a triple bond is counted as 3 bonds.

For example, benzene has two structures having a double bond and a single bond between two carbon atoms.

$$\text{Bond order} = \frac{2+1}{2} = 1.5$$

Carbonate ion, CO_3^{2-} has three resonating structures as:



$$\text{Bond order of C and O} = \frac{2+1+1}{3} = 1.33$$

➢ Some misconceptions

There are certain misconceptions about resonance. The following points should be kept in mind :

⇒ The resonating structures (canonical forms) have no real existence.

⇒ It does not mean that the molecule exist for a certain fraction of time in one canonical form and for other fraction of time in another canonical form.

⇒ There is no equilibrium between the canonical forms like tautomeric forms (Keto-enol forms) in tautomerism.

⇒ The real molecule cannot be depicted by a single Lewis structure.

POLARITY OF BONDS

The existence of a hundred percent ionic bond or a covalent bond represents an ideal situation. However, in reality no bond is completely covalent or completely ionic. Even in the case of covalent bond between two hydrogen atoms, there is some ionic character.

When a covalent bond is formed between two similar atoms, the shared pair of electrons is equally attracted by the two atoms. As a result of this, the electron pair is situated exactly in between two identical nuclei as shown below :

H : H :Cl : Cl: :F : F:

The common examples are H_2, O_2, N_2, Cl_2, F_2, etc. The bond is known as *non-polar covalent bond.* On the other hand, if the atoms forming bonds are different, the electron attracting powers of the two atoms in a bond may differ. Consequently, the shared pair will be displaced towards the atom having more electronegativity. We have learnt in previous unit that, the electronegativity measures the tendency of an atom to attract the shared pair of electrons towards itself in a covalent bond. For example, let us consider a molecule of HCl. The electronegativities of Cl and H are 3.0 and 2.1 respectively. Due to the larger electronegativity of chlorine, the bonding pair will be attracted more towards chlorine atom. Therefore, chlorine atom will experience more negative charge around it and the other atom will experience as if it has lost some of its negative charge. Due to this, the chlorine end of the molecule will

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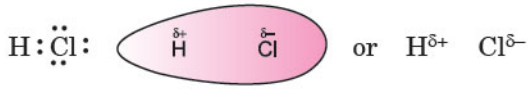
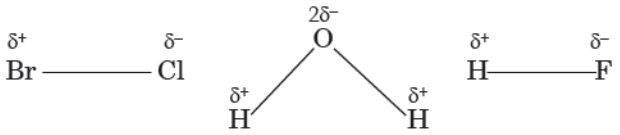
acquire *slightly negative charge* and the hydrogen end will have *slightly positive charge*. These are represented as δ – and δ+ (delta meaning small) charges. Such molecules having two oppositely charged poles are called **polar molecules** and the bond is said to be **polar covalent bond.** The magnitude of electronegativity difference reflects the degree of polarity. *Greater the difference in the electronegativities of the atoms forming the bond, greater will be the charge separation and hence greater will be the polarity of the molecule.*



or $H^{\delta+}$ $Cl^{\delta-}$

Similarly, molecules such as BrCl, H_2O, HF, etc. are also polar molecules.



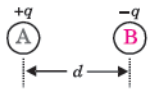
Dipole Moment—A Measure of Degree of Polarity

As studied above, in the case of polar molecules, the centre of negative charge does not coincide with the centre of positive charge. Such molecules having two equal and opposite charges separated by certain distance are said to possess **electric dipole**. For example, a molecule like HCl behaves like a dipole. Since the molecule as a whole is electrically neutral, the negative charge is always equal to the positive charge. The degree of polarity in the molecule is expressed by a term known as dipole moment. **Dipole moment** is defined as

the product of the magnitude of the charge and the distance of separation between the charges.

It is usually represented by a Greek letter 'μ'. Mathematically,

dipole moment = charge (q) × distance of separation



or $\mu = q \times d$

where q = charge on any of the atoms

d = distance between the atoms

Since the charge 'q' is of the order of 10^{-10} e.s.u and the intermolecular distance 'd' is of the order of 10^{-8} cm (*i.e.*, 1Å), therefore, the dipole moment 'μ' is of the order of $10^{-10} \times 10^{-8}$ *i.e.*, 10^{-18} esu cm. This quantity is called 1 Debye and is denoted by the symbol 'D'. Thus,

$$1D = 1 \times 10^{-18} \text{ esu cm}$$

For example, dipole moment of HCl molecule is 1.03 D and that of H_2O is 1.85 D.

In SI units, dipole moment is expressed in the units of Cm; as

$$1 \text{ esu} = \frac{1.602 \times 10^{-19} \text{C}}{4.803 \times 10^{-10}} = 3.335 \times 10^{-10} \text{C}$$

and $1 \text{ cm} = 10^{-2} \text{ m}$

$1 \text{ D} = 10^{-18} \text{ esu cm}$

$= 10^{-18} (3.335 \times 10^{-10} \text{C}) \times (10^{-2} \text{ m})$

$= \mathbf{3.335 \times 10^{-30} \text{ Cm}}$

Dipole moment is a vector quantity and is represented by a small arrow with tail at the positive centre and head pointing towards the negative centre.

+ (end) ⟶ – (end)

For example, the dipole of HCl may be represented as :

H ⟷ Cl

The shift in electron density is symbolised by crossed arrow (+⟶) above the Lewis structure to indicate the direction of the shift.

Dipole Moment and Molecular Structure

(*a*) Diatomic molecules. A diatomic molecule has two atoms bonded to each other by a covalent bond. In such a molecule, the dipole moment of the bond (known as bond dipole) also gives the dipole moment of the molecule. Thus, a diatomic molecule is polar, if the bond formed between the atoms is polar. For example, dipole moment of HCl molecule is the same as that of H—Cl bond, (μ = 1.07 D).

Greater the electronegativity difference between the atoms, more will be the dipole moment of such molecules. For example, the dipole moment of hydrogen halides decreases with decreasing electronegativity of the halogen atom.

	H—F	H—Cl	H—Br	H—I
Electronegativity of halogen atom	4.0	3.0	2.8	2.5
Dipole moment	1.78 D	1.07 D	0.79 D	0.38 D

(*b*) Polyatomic molecules. In case of polyatomic molecules (containing more than two atoms), the dipole moment not only depends upon the individual dipole moments of the bonds (called bond dipoles) but also on the spatial arrangement of the various bonds in the molecule. In such cases, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. For example, carbon dioxide (CO_2) and water (H_2O) are both triatomic molecules but dipole

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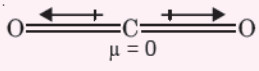
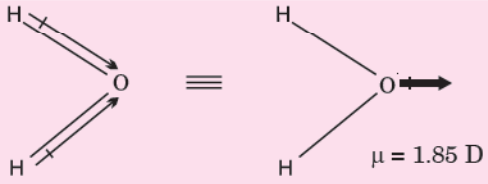
moment of carbon dioxide is zero whereas, that of water is 1.84 D. This can be explained on the basis of their structures.

Carbon dioxide is a linear molecule in which the two C ═O bonds are oriented in the opposite directions at an angle of 180°. The dipole moment of each C ═ O bond is 2.3 D but due to linear geometry of CO_2, the dipole moment of one C ═ O bond cancels that of another. Therefore, the resultant dipole moment of the molecule is zero.



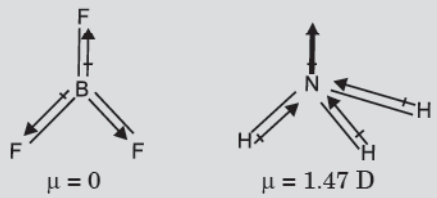
Hence, CO_2 is a non-polar molecule. On the other hand, water molecule has a bent structure in which the



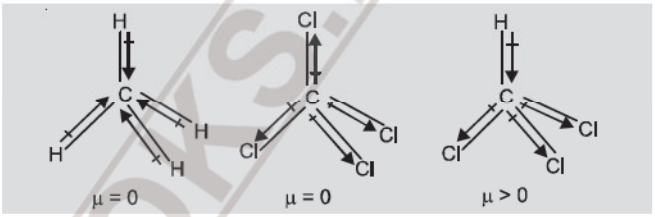
two O—H bonds are oriented at an angle of 104.5°. The dipole moment of water is 1.85 D (or 1.85 × 3.335 × 10^{-30} Cm = 6.17 × 10^{-30} Cm) , which is the resultant of the dipole moments of two O—H bonds.

The dipole moment in case of BeF_2 is zero. This is because the molecule is linear and the two equal bond dipoles point in opposite directions. These bond dipoles cancel the effect of each other giving a net zero dipole moment.

Let us consider tetra-atomic molecules such as BF_3 and NH_3. The dipole moment of BF_3 molecule is zero while that of NH_3 is 1.47 D or 4.90 × 10^{-30} Cm. This suggests that BF_3 molecule has symmetrical structure in which the three B—F bonds are oriented at an angle of 120° to one another. The three bonds lie in one plane and the dipole moments of these bonds cancel one another giving net dipole moment equal to zero. On the other hand, the ammonia molecule has pyramidal structure. The individual bond dipole moments of three N—H bonds give the resultant dipole moment of NH_3 molecule as 1.47 D.



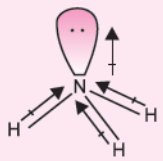
Thus, it may be concluded that *the presence of polar bonds in a polyatomic molecule does not mean that the molecule as a whole will always have dipole moment*. In some cases, the arrangement of individual bonds in the molecule is such that the net dipole moment of the molecule is zero. For example, as discussed earlier, the net dipole moments of carbon dioxide and boron trifluoride molecules are zero. Similarly, the dipole moments of methane and carbon tetrachloride molecules are zero because of the symmetrical tetrahedral shapes of these molecules. However, the dipole moment of $CHCl_3$ (chloroform) is not zero because all the bonds are not same. The resultant of bond dipole moments of three C—Cl bonds is not cancelled by bond dipole moment of C—H bond.



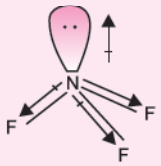
R.U. Curious...

❑ NH_3 and NF_3 molecules present an interesting case in relation to net dipole moment

▶ Both these molecules have pyramidal shape with one lone pair on nitrogen atom. Fluorine is more electronegative than hydrogen and therefore, the N–F bonds should be more polar than N–H bonds. Consequently, the resultant dipole moment of NF_3 should be much larger than that of NH_3. However, the dipole moment of ammonia (μ = 1.47 D) is larger than that of NF_3 (μ = 0.24 D). The anomalous behaviour can be explained due to the presence of lone pair on nitrogen. In case of NH_3, nitrogen is more electronegative than H [electronegativity of N(3.0) and of H(2.1)] and therefore, the dipole of N–H bond is from H to N. The orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the three N–H bonds. Therefore, it adds on the resultant dipole moment of the N–H bonds. On the other hand, in case of NF_3, fluorine is more electronegative than nitrogen [electronegativity of F(4.0) and of N(3.0)] and therefore, the dipole of N–F bond is from N to F. The orbital dipole is in the opposite direction to the resultant dipole moment of the three N–F bonds. Thus, the lone pair moment cancels the resultant N–F bond moments as shown in figure. Consequently, the dipole moment of NF_3 is low.



μ = 1.47 D
(or 4.90 × 10^{-30} Cm)



μ = 0.24 D
(or 0.80 × 10^{-30} Cm)

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The dipole moments of some molecules are given in Table 6.

Table 6. Dipole moments of some molecules.

Type of molecule	Example	Dipole moment μ (D)	Geometry
AB	HF	1.78	Linear
	HCl	1.07	Linear
	HBr	0.79	Linear
	HI	0.38	Linear
	H_2	0	Linear
AB_2	H_2O	1.85	Bent
	H_2S	0.95	Bent
	CO_2	0	Linear
	BeF_2	0	Linear
	CS_2	0	Linear
AB_3	NH_3	1.47	Trigonal pyramidal
	NF_3	0.24	Trigonal pyramidal
	BF_3	0	Trigonal planar
AB_4	CH_4	0	Tetrahedral
	$CHCl_3$	1.04	Tetrahedral
	CCl_4	0	Tetrahedral

Importance of Dipole Moment

Dipole moment plays very important role in understanding the nature of chemical bond. A few applications are given below :

***(i)* Distinction between polar and non-polar molecules.** The measurement of dipole moment can help us to distinguish between polar and non-polar molecules. Non-polar molecules have zero dipole moment while polar molecules have some value of dipole moment. For example, H_2 molecule with zero dipole moment is non-polar molecule while HCl molecule having dipole moment of 1.07 D is a polar molecule. Some other examples are given below :

Non-polar molecules (Dipole moment = 0)		Polar molecules	
H_2	CO_2	H_2O	1.85 D
O_2	BeF_2	HF	1.78 D
Cl_2	BF_3	HCl	1.07 D
N_2	CH_4	H_2S	0.95 D

***(ii)* Degree of polarity in a molecule.** Dipole moment measurement also gives an idea about the degree of polarity specially in a diatomic molecule. The greater the dipole moment, the greater is the polarity in such a molecule. For example, HF (1.78 D) is more polar than HCl (1.07 D).

***(iii)* Shapes of molecules.** As already discussed, in case of molecules containing more than two atoms, the dipole moment not only depends upon the individual dipole moments of the bonds but also on the arrangement of bonds. Thus, dipole moment is used to find the shapes of molecules. For example, the dipole moment of water is 1.85 D while that of carbon dioxide is zero. This means that carbon dioxide is a linear molecule in which the individual dipole moments of two CO bonds cancel each other. On the other hand, water is not linear but it has angular shape as shown above, having the resultant dipole moment of two bond dipoles as 1.84 D.

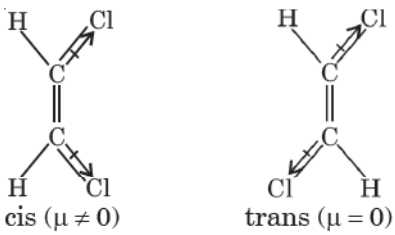
(iv)* Ionic character in a molecule.** Knowing the electronegativities of atoms involved in a molecule, it is possible to predict the nature of chemical bond formed. If the difference in electronegativities of two atoms is large, the bond will be highly polar. As an extreme case, when the electron is completely transferred from one atom to another, an ionic bond is formed. Therefore, the ionic bond is regarded as an extreme case of covalent bond. The greater the difference in electronegativities of the bonded atoms, the higher is the ionic character. It has been observed that ***when the electronegativity difference between two atoms is 1.7, then the bond is 50% ionic and 50% covalent. If the electronegativity difference is more than 1.7, then the chemical bond formed is predominantly ionic (more than 50% ionic character) and if the difference is less than 1.7, the bond formed is mainly covalent. Larger the electronegativity difference, larger will be the ionic character. For example, bond between Cs (0.7) and F (4.0) is more ionic than bond between Li (1.0) and F (4.0). On the other hand, the bond between C (2.5) and H (2.1) or Cl (3.0) is almost covalent because the electronegativity difference between bonding atoms is small.

The percentage of ionic character can be calculated from the ratio of the observed dipole moment to the dipole moment for the complete electron transfer (100% ionic character). For example, in HCl molecule, the observed dipole moment is 1.07 D and its bond length is 1.275 Å. Assuming 100% ionic character, the charge developed on H and Cl atoms would be 4.8×10^{-10} esu. Therefore, dipole moment for 100% ionic character will be

$$\mu_{ionic} = q \times d = 4.8 \times 10^{-10} \text{ esu} \times 1.275 \times 10^{-8} \text{ cm}$$
$$= 6.12 \times 10^{-18} \text{ esu cm} = 6.12 \text{ D}$$
$$(1 \text{ D} = 10^{-18} \text{ esu cm})$$

$$\therefore \quad \% \text{ ionic character} = \frac{\text{Observed dipole moment}}{\text{Dipole moment for complete ionic character}} \times 100$$
$$= \frac{1.07}{6.12} \times 100 = 17.48\%$$

***(v)* Distinguish between cis- and trans-isomers.** Dipole moment measurements help to distinguish between *cis*- and *trans*- isomers because cis- isomer has usually higher dipole moment than trans isomer. For example, in trans-isomer of 1, 2-dichloroethene, the dipole moment is less because the bond moments of C—Cl bonds cancel each other.



cis ($\mu \neq 0$) trans ($\mu = 0$)

***(vi)* Distinguish between *ortho, meta* and *para* isomers.** Dipole moment measurements help to distinguish between *o*-, *m*- and *p*- isomers because the dipole moment of *p*-isomer is zero and that of *o*-isomer is more than that of m-isomer. For example, for dichlorobenzene :

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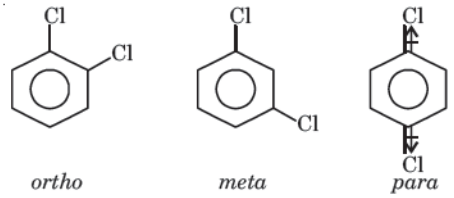

ortho $\mu = 2.54$ D | *meta* $\mu = 1.48$ D | *para* $\mu = 0$

Partial Covalent Character in Ionic Bonds

Ionic and covalent bonds are two extreme types of bonds. In fact, most of the heteronuclear bonds have intermediate character. Even in the case of pure ionic compounds, there is some degree of covalent character. When two oppositely charged ions A^+ and B^- are brought together, the positive ion attracts the outermost electrons of the negative ion. This results in distortion of electron clouds around the anion towards the cation. ***This distortion of electron cloud of the negative ion by the positive ion is called* polarisation**. If the polarisation is small, the bond is mainly ionic. On the other hand, if the degree of polarisation is large, electron cloud is drawn more from the negative ion to the positive ion. Consequently, the charges on the ions become less (negative becomes less, +ve charge also becomes less because some of it is neutralised by the electron cloud of anion). This decreases the ionic character of the bond and favours the covalent character. The polarisation of an anion by cation is shown below. In Fig. (a), the two ions are shown without any polarisation, assuming that the bond is completely ionic. This represents an ideal ion

(a) (b)

pair. The positive ion polarises the negative ion and draws electrons towards itself. As a result of polarisation, there is decrease of positive charge on the cation and decrease of negative charge on the anion. This leads to **covalent character**. Obviously, **if polarisation is more, larger will be covalent character of the bond**. Thus, the type of bond depends upon the degree of polarisation.

- *If there is no polarisation, the bond is mainly ionic.*
- *If the degree of polarisation is small, the bond will be ionic with some covalent character and*
- *If the polarisation is more, the covalent character becomes predominent.*

The extent of polarisation depends on both the ions as :

(i) the power of the cation to distort or polarise the anion.

(ii) the susceptibility of the anion to get polarised by the cation.

The tendency of the cation to polarise and the polarisability of the anion are summarised in the following rules known as **Fajan rules**.

Fajan Rules

1. Small size of the cation. *Smaller the size of the cation, greater is its polarising power.* The polarising power of a cation decreases with increase in its size. The small cations have high electron density and therefore, they tend to distort or polarise the electron cloud of the anion to greater extent. Therefore, the compounds containing small cations will have more covalent character. This easily explains that LiCl is more covalent than NaCl and KCl.

2. Large size of anion. *Polarisation increases with increase in size of anion.* This is because the electron cloud on the bigger anion will be held less firmly by its nucleus and, therefore, would be more easily deformed towards the cation. Thus, larger the anion, the higher will be its polarisability and more will be covalent character in its compounds. Therefore, the anions such as I^-, Br^-, S^{2-}, Se^{2-}, etc. are easily polarisable and have larger tendency to induce covalent character in ionic compounds.

Therefore, covalent character of lithium halides follows the order : Li I > Li Br > Li Cl > Li F

3. Large charge on cation or anion. *Larger the charge on cation greater is polarising power and larger the charge on anion greater is its tendency to get polarised.* For example, Na^+ and Ca^{2+} have almost similar ionic radii but $CaCl_2$ has higher covalent character than NaCl because of higher charge on Ca^{2+} ion. Consequently the melting point of $CaCl_2$ is less than that of NaCl.

Compound	Radius	m.pt (°K)
NaCl	Na^+ : 0.95 Å	1073
$CaCl_2$	Ca^{2+} : 0.99 Å	1045

4. Electronic configuration of the cation : Cations with 18 electrons shell configuration (known as *pseudo inert gas configuration*) cause greater polarisation than the cations with 8 electrons shell configuration with the same size and charge. This is due to the fact that in case of 18 electrons shell ion, there are 10 *d* electrons in addition to eight *s*-and *p*–electrons. The d-electrons donot shield the nuclear charge effectively and therefore, they have increased effective nuclear charge. Consequently, these ions behave as though they are under the influence of greater nuclear charge and polarise the anion to a greater extent. Therefore, such compounds will have more covalent character.

For example, if we compare the ions of same size; Na^+ and Cu^+, Na^+ has eight electrons shell configuration ($2s^2 2p^6$) while Cu^+ has 18 electrons shell configuration ($3s^2\ 3p^6\ 3d^{10}$). The Cu^+ ion polarize the anion more than Na^+ ion. As a result, copper chloride, CuCl is slightly covalent and therefore, insoluble in water whereas NaCl is ionic and highly soluble in water. The covalent character of CuCl in comparison to NaCl is also supported by its low melting point. Melting point of CuCl is 705 K while that of NaCl is 1073 K.

Thus, according to Fajan rules, the covalent character will be favoured by :

(i) Small size of cation

(ii) Large size of anion

(iii) High charge of cation and anion

(iv) The cation having 18-electrons shell.

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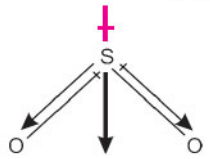
SOLVED EXAMPLES

Example 8.

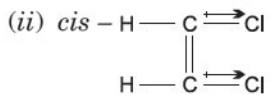
Sketch the bond moments and resultant dipole moments in

(i) SO_2 (ii) cis-and trans of $C_2H_2Cl_2$

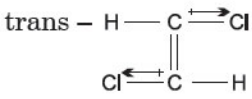
Solution: *(i)*



(ii)



Resultant $\mu \neq 0$



Resultant $\mu = 0$

Example 9.

Calculate the percentage ionic and covalent character of HF molecule having bond distance = 0.92 Å and dipole moment = 1.78 D

Solution:

Dipole moment of the molecule assuming 100% ionic character :

$$\mu_{ionic} = q \times r$$

$$q = 4.8 \times 10^{-10} \text{ esu}, \quad r = 0.92 \times 10^{-8} \text{ cm}$$

$$\mu_{ionic} = 4.8 \times 10^{-10} \times 0.92 \times 10^{-8}$$

$$= 4.416 \times 10^{-18} \text{ esu cm} = 4.416 \text{ D}$$

Observed dipole moment, $\mu_{observed} = 1.78$ D

Percentage ionic character

$$= \frac{\mu_{observed}}{\mu_{ionic}} = \frac{1.78}{4.416} \times 100 = \mathbf{40.3\ \%}$$

Percentage covalent character $= 100 - 40.3$

$$= \mathbf{59.7\ \%}$$

Example 10.

The dipole moment of HBr molecule is 0.78 D and the bond distance is 1.41 Å. Calculate the fractional charges δ on H and Br atoms in HBr (electronic charge, $e = 4.8 \times 10^{-10}$ esu).

Solution: Dipole moment, $\mu = q \times r$

$\mu = 0.78$ D $= 0.78 \times 10^{-18}$ esu. cm,

$r = 1.41 \times 10^{-8}$ cm

$$\therefore \quad q = \frac{0.78 \times 10^{-18} \text{ esu cm}}{1.41 \times 10^{-8} \text{ cm}} = 0.55 \times 10^{-10} \text{ esu.}$$

$$\text{Now, fraction of charge} = \frac{\text{Charge present}}{\text{Electronic charge}}$$

$$\delta = \frac{q}{e} = \frac{0.55 \times 10^{-10}}{4.8 \times 10^{-10}} = 0.11$$

$$\therefore \quad \mathbf{\delta_{H^+} = 0.11, \ \delta_{Br^-} = -0.11}$$

Example 11.

The dipole moment of lithium hydride is 1.962×10^{-29} cm and interatomic distance between Li and H in the molecule is 0.1592 nm. Calculate the percentage ionic character of the molecule.

Solution: Dipole moment of the molecule assuming 100% ionic character,

$$\mu_{ionic} = q \times d$$

$$q = 1.602 \times 10^{-19} \text{C}, \ d = 0.1592 \text{ nm}$$

$$= 0.1592 \times 10^{-9} \text{ Cm}$$

$$\therefore \quad \mu_{ionic} = (1.602 \times 10^{-19} \text{ C}) \times (0.1592 \times 10^{-9} \text{ m})$$

$$= 2.55 \times 10^{-29} \text{ Cm}$$

$$\mu_{observed} = 1.962 \times 10^{-29} \text{ Cm}$$

$$\therefore \quad \% \text{ ionic character} = \frac{\mu_{observed}}{\mu_{ionic}} \times 100$$

$$= \frac{1.962 \times 10^{-29} \text{ Cm}}{2.55 \times 10^{-29} \text{ Cm}} \times 1000$$

$$= \mathbf{76.94\%}$$

Practice Problems

11. Which molecule is polar in each of the following pairs ?

(i) HF, F_2 *(ii)* CO_2, H_2O

(iii) N_2, NH_3 *(iv)* CH_4, CH_3Cl.

12. Which of the following hydrogen halides has the most polar bond ?

(i) HF *(ii)* HCl

(iii) HBr *(iv)* HI.

13. Which of the following molecules have electric dipoles ?

(i) CCl_4 *(ii)* $CHCl_3$ *(iii)* CH_2Cl_2

(iv) CH_3Cl *(v)* CH_4.

14. Predict the dipole moment of :

(i) a molecule of the type AX_2 having a linear geometry.

(ii) a molecule of the type AX_4 having tetrahedral geometry.

(iii) a molecule of the type AX_2 having angular geometry.

(iv) a molecule of the type AX_4 having square planar geometry.

Answers to Practice Problems

11. *(a)* HF *(b)* H_2O *(c)* NH_3 *(d)* CH_3Cl

12. *(a)* HF

13. $CHCl_3$, CH_2Cl_2, CH_3Cl

14. *(i)* zero *(ii)* zero *(iii)* appreciable dipole moment *(iv)* zero

GEOMETRY OR SHAPES OF MOLECULES

The different atoms in a molecule have definite geometric arrangements in space around the central atom. ***This definite relative arrangement of the bonded atoms in a molecule*** is known as the **geometry** or **shape of the molecules.**

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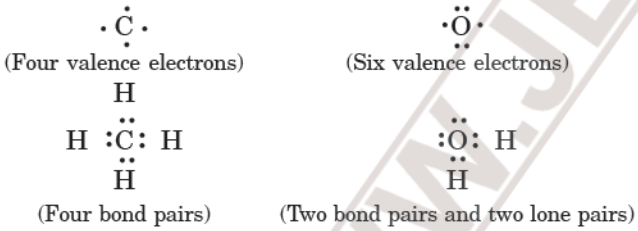
VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

In 1940, Sidgwick and Powell proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and refined by Nyholm and Gillespie in 1957. They suggested that the shapes of molecules can be determined by the number of electron pairs (bonding as well as non-bonding) in the valence shell of the central atom and proposed a theory known as **valence shell electron pair repulsion (VSEPR) theory**. The basic idea of this theory is that *bonded atoms in a molecule adopt that particular arrangement in space around the central atom which keeps them on an average as far apart as possible.*

Postulates of VSEPR Theory. The main postulates of VSEPR theory are :

1. The shape of a molecule depends upon the number of valence shell electron pairs (whether bonded or not) around the central atom.

In the formation of a bond, the central atom shares its valence electrons with the surrounding atoms. However, in certain cases, all the valence shell electrons may not take part in the bond formation. The electrons left in the valence shell without forming bonds exist as **lone pairs**. For example, in methane, (CH_4), carbon uses all the four valence electrons in forming four bond pairs. On the other hand, in water (H_2O), the central oxygen atom has ($1s^2\ 2s^2 2p^4$) six valence electrons. The hydrogen atom shares two of these six valence electrons in bond formation leaving four electrons as two lone pairs. Thus, in methane, there are four bond pairs around carbon, while oxygen in water has two bond pairs and two lone pairs around it.



(Four valence electrons) (Six valence electrons)

(Four bond pairs) (Two bond pairs and two lone pairs)

2. Electron pairs in the valence shell tend to repel one another because their electron clouds are negatively charged.

3. The electron pairs tend to occupy positions in space that minimize repulsions. Therefore, they *try to stay as far apart as possible to acquire a state of minimum energy or maximum stability.*

4. The valence shell is taken as a sphere with the electron pairs localizing on the spherical surface at maximum distances from one another.

5. The electron pairs in multiple bonds are treated as a single unit like a single electron pair. In other words, two or three electron pairs of a double bond or a triple bond respectively are considered as a single super pair equivalent to a single electron pair.

6. Repulsion between the lone pair and lone pair of electrons is different than that between two bond pairs or one lone pair and one bond pair. The repulsive interactions decrease in the order :

Lone pair — Lone pair > Lone pair — Bond pair > Bond pair —Bond pair.

The presence of lone pairs in addition to bond pairs, will result in certain distortions in the regular geometry of molecules.

7. Repulsive forces decrease sharply with increasing angle between the electron pairs. They are strong at 90°, weaker at 120° and weakest at 180°.

Nyholm and Gillespie (1957) improved VSEPR model by pointing to the important difference between lone pairs and bond pairs. They suggested that the repulsive interactions between the bonded and the lone pairs of electrons are different. This can be understood as follows :

The orbital of bonded electron pair is under the influence of two nuclei and most of the electron cloud is oriented between the nuclei of the two atoms. On the other hand, the lone pair of electrons is under the influence of only one nucleus and, therefore, its electron cloud is spread out and tends to occupy more space. For example, Fig. 4 shows a molecule of ammonia (NH_3) in which there are three bond pairs and one lone pair. Since the lone pair is flatter and occupies more space around the central atom, it can interact more and, therefore, it will repel the electron pairs in the neighbouring orbitals strongly than do the electrons in the bonded orbital. Obviously, the repulsion between two lone pairs would be the largest and will be lesser if one of them is bond pair and the least if both are bond pairs.

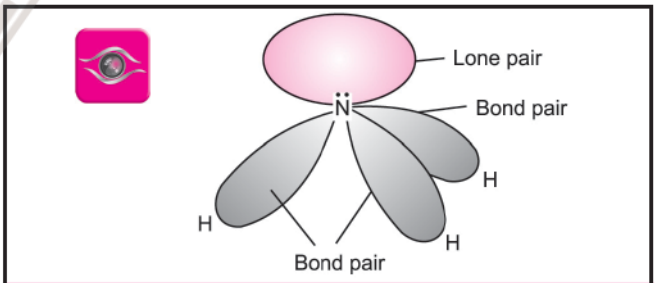


Fig. 4. Lone pair and bond pairs in NH_3 molecule.

Thus, *the repulsive interactions between different pairs of electrons* will decrease in the order :

Lone pair—Lone pair > Lone pair—Bond pair > Bond pair—Bond pair

Shapes of molecules on the basis of VSEPR theory

This theory is very simple to use. *In this theory no distinction is made between s-and p-electrons. We take into account only the number of electron pairs present in the valence shell of the central atom.* Thus, the particular geometry of a molecule depends upon the number of electron pairs around the central atom. For example, if there are two electron pairs around the central atom, the only way to keep them as far apart as possible is to arrange them at an angle of 180° to each other. The molecule in such a case will adopt **linear** geometry.

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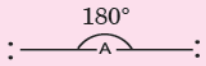
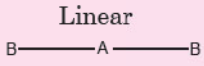
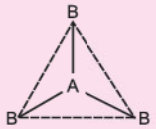
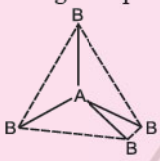
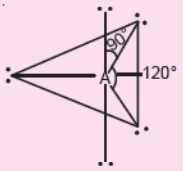
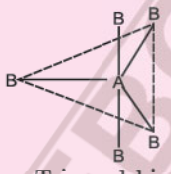
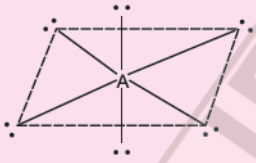
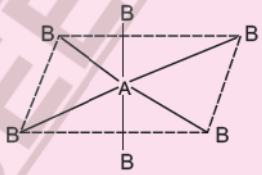
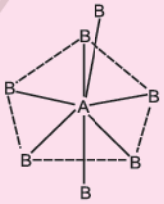
Similarly, for three electron pairs around the central atom, the molecule adopts **trigonal planar** geometry and for four electron pairs around the central atom, the molecule adopts **tetrahedral** geometry.

The molecules having five electron pairs around the central atom have **trigonal bipyramidal** geometry. The molecules having six electron pairs around the central atom have **octahedral** geometry.

The goemetries of molecules based on the number of electron pairs is given in Table 7.

Table 7. Geometries of molecules on the basis of VSEPR theory.

Number of electron pairs around central atom	Arrangement of electron pairs	Molecular Geometry	Bond angles	Examples
2		 Linear	180°	BeF_2, $BeCl_2$, BeH_2, $ZnCl_2$
3		 Trigonal planar	120°	BF_3, $AlCl_3$
4		 Tetrahedral	109.5°	CH_4, SiH_4, SiF_4, NH_4^+
5		 Trigonal bipyramidal	three 120° two 90°	PF_5, $SbCl_5$
6		 Octahedral	90°	SF_6, TeF_6
7		 Pentagonal bipyramidal	90°, 72°	IF_7

Let us illustrate this theory by considering a few examples :

A. Shapes of Molecules containing Bond Pairs only

1. Shape of BeF_2 molecule : Linear

In BeF_2, the central Be-atom (Z = 4; $1s^2\ 2s^2$) has two electrons in the valence shell. In the formation of BeF_2, each of these valence electrons is shared by two flourine atoms. As a result, the Be-atom is surrounded by two bond pairs of electrons [Fig. 5]. Therefore, the geometry of BeF_2 molecule is **linear** as shown and the bond angle is 180°.

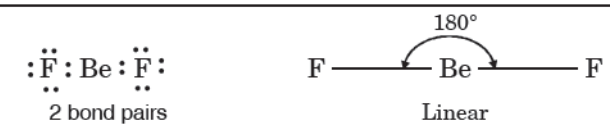


Fig. 5. Shape of BeF_2 molecule having two electron pairs around Be-atom.

Other molecules such as $BeCl_2$, $ZnCl_2$, $HgCl_2$ have linear shape.

2. Shape of BF_3 molecule : Trigonal planar

The central atom, boron (Z = 5, $1s^2\ 2s^2\ 2p^1$) has *three valence electrons*. In the formation of BF_3

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molecule, each electron in the valence shell of B-atom forms a bond pair with F-atom. As a result, the central boron atom is surrounded by three bond pairs and the molecule adopts **trigonal planar** geometry. In this geometry, all the F—B—F bond angles are of 120°. This geometry is planar because the three F-atoms and B-atom lie in the same plane.

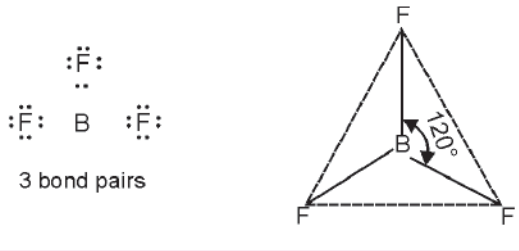

Fig. 6. Shape of BF_3 molecule having three electron pairs around B-atom.

Molecules such as BCl_3, $AlCl_3$, etc. have same shape.

3. Shape of CH_4 molecule : Tetrahedral

The central atom, carbon (Z = 6, $1s^2 2s^2 2p^2$) has four valence electrons. All the four valence electrons are bonded to four hydrogen atoms forming four bond pairs around the central carbon atom. These four electron pairs, trying to remain as far apart as possible, adopt **tetrahedral structure.** In this geometry, all the H—C—H bond angles are of 109°28′ (or approximately 109.5°).

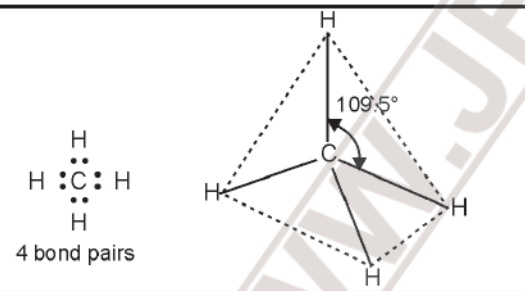

Fig. 7. Shape of CH_4 molecule having four electron pairs around C-atom.

Other examples of tetrahedral molecules are SiF_4, CCl_4, SiH_4, NH_4^+, etc.

4. Shape of PCl_5 molecule : Trigonal bipyramidal

In PCl_5, the central atom, P (Z = 15 ; $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^3$) has five valence electrons. It forms five bond pairs with five Cl-atoms to form a molecule of PCl_5. Since there are five electron pairs around the central phosphorus atom and therefore, it has **trigonal bipyramidal** geometry as shown in Fig. 8. In this geometry, all the bond angles are not equal. Three electron pairs are in the same plane at an angle of 120°, while other two are perpendicular to the plane, both making an angle of 90° with the plane. Thus, in this arrangement three bond angles are of 120° each and two are of 90° each.

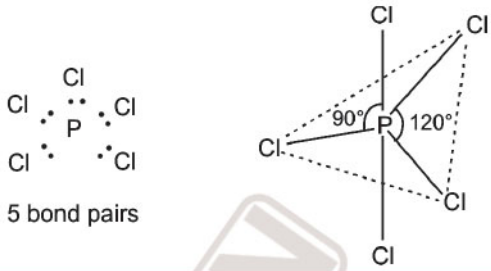

Fig. 8. Shape of PCl_5 molecule having five electron pairs around P-atom.

In this geometry, all five P—Cl bonds are not equal. The three bonds lying in the trigonal plane are called **equatorial bonds.** Of the remaining two bonds, one lies above and the other below the equatorial plane, both making an angle of 90° with the plane. These bonds are called **axial bonds.** It has been observed that axial bonds are slightly longer than equatorial bonds in this geometry. PF_5 has the same shape.

The larger bond length of axial bonds than equatorial bonds can be explained in terms of the repulsive forces between electron pairs due to different bond angles. Let us count the repulsive interactions of an axial and an equatorial electron pair. As shown in the figure (Fig. 9) the electron pair of axial bond (say 1) is being repelled by three electron pairs (of bonds 2,3 and 4) at 90° and one (of bond 5) at 180°. On the other hand, the electron pair of the equatorial bond (say 2) is being repelled by two electron pairs (1 and 5) at 90° and two (3 and 4) at 120°. Now, we know that the repulsion between electron pairs decreases with increasing angle between them. Therefore, the repulsion between electron pairs at 120° and 180° may be neglected in comparison to those at 90°. Thus, considering only the repulsions between electron pairs at 90°, we observe that each axial bond is repelled by three electron pairs while each equatorial bond is repelled by two bond pairs. This means that axial bond pair faces greater repulsion from other bonds and therefore, the axial bond is slightly longer than equatorial bond.

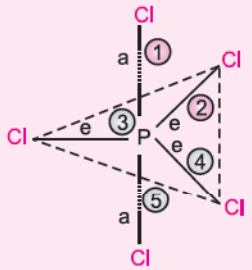

Fig. 9. Axial and equatorial bonds in PCl_5

It may be noted that the structure of PCl_5 molecule is unsymmetrical. As a result, it is less stable and is therefore, highly reactive.

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5. Shape of SF_6 molecule : Octahedral.

In SF_6, the central S-atom (Z = 16 ; $1s^2\ 2s^2\ 2p^6$, $3s^2\ 3p^4$) has *six valence electrons*. Each of these six valence electrons forms bond with F-atom and therefore, the molecule has **octahedral geometry.** In this case, all the bond angles are same and are of 90° each. TeF_6 molecule has same shape.

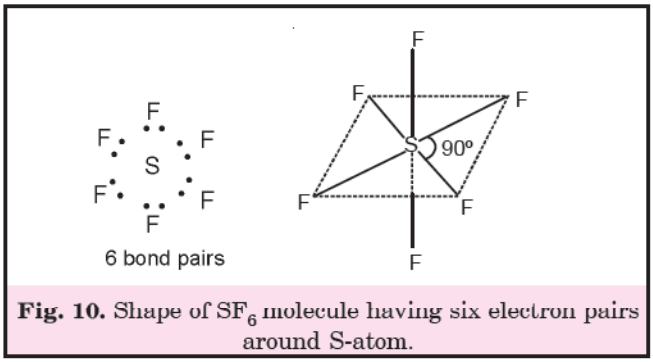

Fig. 10. Shape of SF_6 molecule having six electron pairs around S-atom.

Other examples of octahedral molecules are SeF_6, TeF_6, etc.

6. Shape of IF_7 molecule : Pentagonal bipyramidal

In IF_7, the central atom I (Z = 53, ... $5s^2 5p^5$) has *seven valence electrons*. Each of these seven valence electrons forms bond with F-atom and therefore, the molecule has **pentagonal bipyramidal geometry.** In this case, all the bond angles are not equal. Five electron pairs are in the same plane at an angle of 72°, while other two are perpendicular to the plane both making an angle of 90° with the plane. Thus, in this arrangement five bond angles are of 72° each and two are of 90° each.

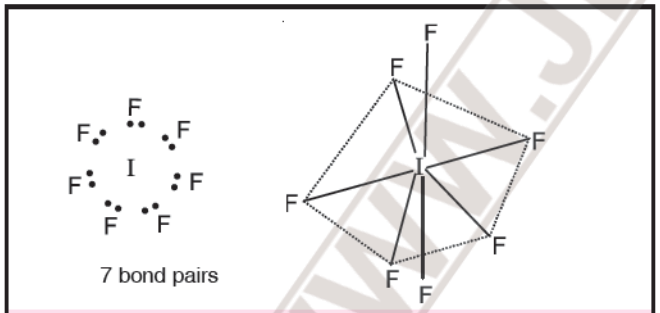

Fig. 11. Shape of IF_7 molecule having seven electron pairs around I atom.

B. Shapes of Molecules containing Lone Pairs and Bond Pairs

Now, let us consider a few molecules containing bond pairs as well as lone pairs.

1. Molecules containing three electron pairs (AB_3 or AB_2L)

If the valence shell of an atom contains three electron pairs, then the molecule has **trigonal planar geometry** (e.g., BF_3). However, if it contains a lone pair in addition to bond pair, the geometry gets distorted. For example, a molecule of the type AB_2L (where L represents a lone pair), has V-shaped geometry as discussed for SO_2 molecule.

Shape of sulphur dioxide (SO_2) molecule.

In SO_2 molecule, there are three electron pairs (two bond pairs and one lone pair).

The three electron pairs should acquire a trigonal planar arrangement with bond angle 120°. Since one of the positions is occupied by a lone pair, the geometry may be described as **angular** or **V-shaped** or **bent shape.**

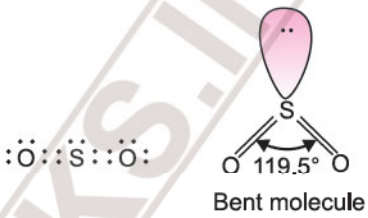

Fig. 12. Shape of SO_2 molecule.

Now, lone pair-bond pair repulsion is more than bond pair-bond pair repulsion. Therefore, bonded pairs of electrons are pushed more closer and the OSO bond angle gets reduced to 119.5° from the value of 120°.

2. Molecules Containing Four Electron Pairs (AB_4, AB_3L, AB_2L_2)

As already learnt, the molecule AB_4 has **tetrahedral** geometry. But if lone pairs are also present in addition to bond pairs, the geometry gets distorted. This may be illustrated by taking two examples :

(*a*) Molecules containing 3 *bp* and 1 *lp* AB_3L. *e.g.*, NH_3

(*b*) Molecules containing 2 *bp* and 2 *lp* AB_2L_2 *e.g.*, H_2O.

(*a*) Molecules containing 3 *bp* and 1 *lp*; AB_3L.

Shape of NH_3 (ammonia) molecule

In ammonia molecule, the central nitrogen atom (Z = 7, $1s^2\ 2s^2\ 2p^3$) has five valence electrons. Three of these valence electrons share electrons with three hydrogen atoms forming three bond pairs around the nitrogen atom. The remaining two electrons are present as a lone pair. Thus, in ammonia, nitrogen is surrounded by **four electron pairs** (three bond pairs and one lone pair). These four electron pairs adopt **tetrahedral geometry.** But all the four electron pairs around nitrogen are not equivalent (three bond pairs and one lone pair) and therefore, ammonia has *distorted tetrahedral* geometry. The bond angle will not be 109.5° but it is 107°. This distortion is due to the presence of one lone pair in addition to bond pairs. As already explained, lone pair-bond pair repulsion is more than bond pair-bond pair repulsion. As a result, the lone pair of electrons will repel the bond pairs strongly and bond angle decreases to 107°. The

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geometry of ammonia molecule is also regarded as **pyramidal** (Fig. 13).

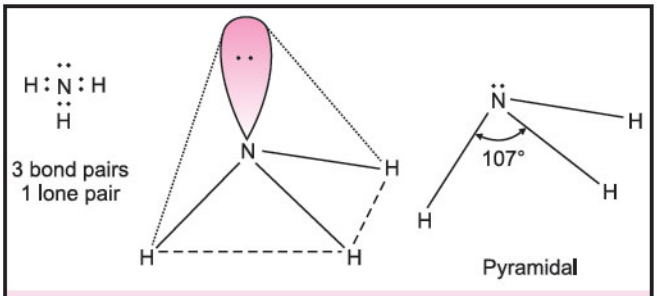

Fig. 13. Shape of NH_3 molecule according to VSEPR theory.

Other molecules with same shape are PCl_3, NF_3, H_3O^+, etc.

(*b*) Molecules containing 2 *bp* and 2 *lp*; AB_2L_2

Shape of H_2O (water) molecule

In the case of water molecule, the central oxygen atom (Z = 8, $1s^2\ 2s^2\ 2p^4$) has six valence electrons. In the formation of water molecule, the electrons form two bond pairs with two hydrogen atoms leaving four electrons as two lone pairs.

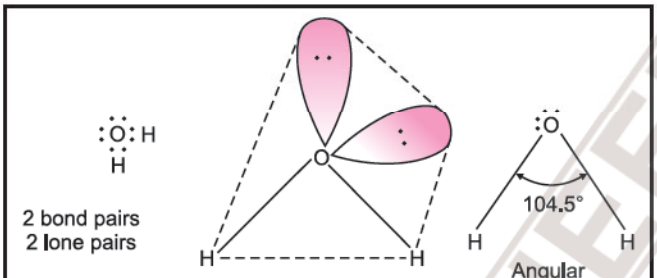

Fig. 14. Shape of H_2O molecule according to VSEPR theory.

The four electron pairs around the central oxygen atom adopt tetrahedral geometry. However, all the four electron pairs around O are not equivalent and therefore, geometry is *distorted tetrahedral*. The bond angle in water molecule is not of 109.5° but it is of 104.5° (Fig. 14). The distortion is due to the presence of two lone pairs in addition to bond pairs. The force of repulsion between lone pair–lone pair is larger than the force of repulsion between two bond pairs of electrons. Thus in water, the two lone pairs of electrons move away from each other while the two O—H bonds are forced closer to each other (even more than N—H bonds in NH_3) resulting in decrease of H—O—H angle to 104.5°. The resulting geometry is regarded as **bent** or **angular.** Other molecules with same shape are H_2S, F_2O, SCl_2, etc.

KEY NOTE

It may be noted here that the central atoms (C, N and O) in three molecules CH_4, NH_3 and H_2O have four electron pairs around the central atom. Therefore, these molecules adopt tetrahedral geometries. But in methane, there is no lone pair, NH_3 molecule has one lone pair while H_2O molecule has two lone pairs in the total of four electron pairs. Due to the presence of lone pairs, NH_3 and H_2O molecules will have distorted geometries, while CH_4 molecule will have regular geometry of tetrahedron. Due to larger lone pair–bond pair repulsion than bond pair–bond pair in NH_3, the bond angle is reduced from 109.5° to 107°. The geometry of NH_3 is **pyramidal.**

Now, in case of H_2O, two lone pairs force the O—H bonds more closely than the N–H bonds in NH_3. So the bond angle decreases to a larger extent *i.e.*, to 104.5°. The geometry of water is regarded as **V-shaped** or **angular**.

3. Molecules Containing Five Electron Pairs (AB_5, AB_4L, AB_3L_2 or AB_2L_3)

When the central atom is surrounded by five electron pairs, the geometry is **trigonal bipyramidal.** However, if one or more bond pairs are replaced by lone pairs, the geometry gets distorted. This may be illustrated by the following examples :

(*a*) Molecules containing 4 *bp* and 1 *lp*. *e.g.*, SF_4.

(*b*) Molecules containing 3 *bp* and 2 *lp*. *e.g.*, ClF_3.

(*c*) Molecules containing 2 *bp* and 3 *lp*. *e.g.*, XeF_2.

(*a*) Molecules containing 4 *bp* and 1 *lp*; AB_4L

Shape of SF_4 (sulphur tetrafluoride) molecule

In this case, sulphur atom (Z = 16 : $3s^2\ 3p^4$) has six valence electrons. In the formation of SF_4, four electrons form four bond pairs and leave two electrons as one lone pair. Thus, five electron pairs around sulphur adopt trigonal bipyramidal geometry in which one position is occupied by a lone pair.

Therefore, SF_4 molecule can have structure *(a)* or structure *(b)* as shown in Fig 15, in which the lone pair is present on axial or equatorial positions respectively. Nyholm - Gillespie modification has helped in predicting accurately the geometry of such molecules containing lone pair of electrons.

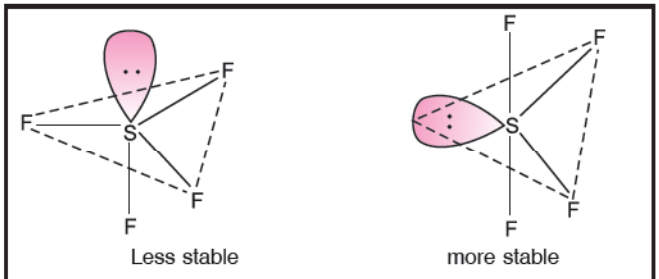

Fig.15. Shape of SF_4 molecule.

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In arrangement *(a)*, the lone pair is in on axial position which has 3 *lp-bp* repulsions at 90°. In structure *(b)* the lone pair is in on equatorial position and there are only two *lp-bp* repulsions. Hence arrangement *(b)* will experience lesser repulsions and will be stable in comparison to arrangement *(a)*. This shape is described as **distorted tetrahedron** or a **folded square** or a **see-saw.** The bond angles in SF_4 are 89° and 117° instead of 90° and 120° respectively.

(b) Molecules containing 3 *bp* and 2 *lp*; AB_3L_2

Shape of ClF_3 (chlorine trifluoride) molecule.

The central chlorine atom (Z = 17 : $3s^2\ 3p^5$) has seven electrons in its valence shell. In the formation of ClF_3, three electrons form three bond pairs and leave four electrons as two lone pairs. Thus, the five electron pairs around chlorine atom adopt trigonal bipyramidal geometry, in which two positions are occupied by lone

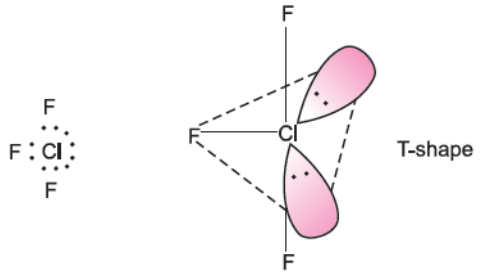
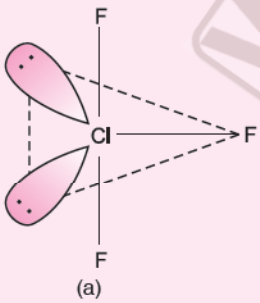


Fig. 16. Shape of ClF_3 molecule according to VSEPR theory.

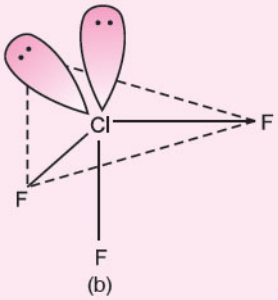
pairs. As already discussed, the lone pair in trigonal bipyramidal geometry experiences more repulsions at axial positions, therefore, both the lone pairs are present at equatorial positions as shown in Fig. 16. The molecule is **T-shaped** and bond angle is 87.6° instead of 90°.

KEY NOTE

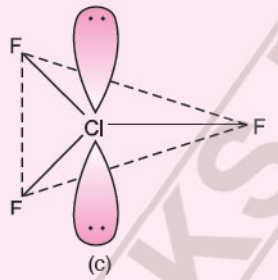
It may be noted that as in case of SF_4, the two lone pairs in ClF_3 may occupy the following three positions:



Two lone pairs on equatorial positions.
Repulsions at 90°
$lp - lp$ =0, $lp - bp$ =4,
$bp - bp$ =2



One lone pair on axial and one lone pair on equatorial positions.
Repulsions at 90°
$lp - lp$ =1, $lp - bp$ = 3,
$bp - bp$ =2



Two lone pairs on axial positions.
Repulsion at 90° :
$lp - lp$ = 0, $lp - bp$ = 6,
$bp - bp$ = 0

It can be seen that **structure, (a) appears to be most stable because** in comparison to structure (b), it has no strong $lp - lp$ repulsion and in comparison to structure (c), it has lesser number of $lp - bp$ repulsions.

(c) Molecules containing 2 *bp* and 3 *lp*; AB_2L_3

Shape of XeF_2 (xenon difluoride) molecule.

Xenon atom has (Z = 54 : $5s^2\ 5p^6$) eight electrons in the valence shell. In the formation of XeF_2, there are two bond pairs and three lone pairs. These five electron pairs adopt trigonal bipyramidal geometry with three positions occupied by lone pairs. Since the three lone pairs are present at the corners of an equilateral triangle, the net repulsion on the bonds due to lone pairs is zero. Thus, the molecule has **linear geometry.**

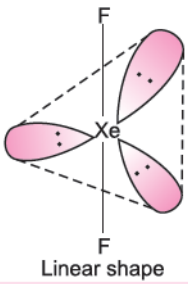


Fig. 17. Shape of XeF_2 molecule.

4. Molecules containing six Electron Pairs (AB_6, AB_5L, AB_4L_2)

When the central atom is surrounded by six electron pairs, the geometry is octahedral. However, if one or more lone pairs are present in addition to bond pair, the geometry gets distorted. This may be illustrated by the following examples :

(*a*) Molecules containing 5 *bp* and 1 *lp e.g.*, BrF_5.
(*b*) Molecules containing 4 *bp* and 2 *lp e.g.*, XeF_4.

(a) Molecules containing 5 *bp* and 1 *lp*; AB_5L

Shape of BrF_5 (bromine pentafluoride) molecule

The central bromine atom (Z = 35, $4s^2\ 4p^5$) has seven valence electrons. In the formation of BrF_5, it has five bond pairs and one lone pair. The six electron pairs

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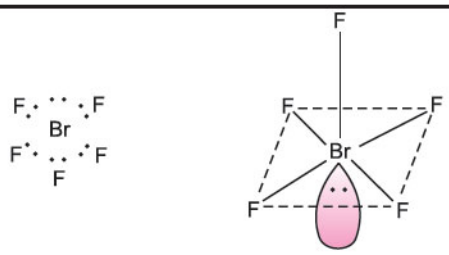
has octahedral geometry in which one of the positions is occupied by a lone pair. Since all the six positions in octahedral geometry are equivalent, therefore, lone pair may be placed on any position (Fig. 18).



Square pyramidal shape

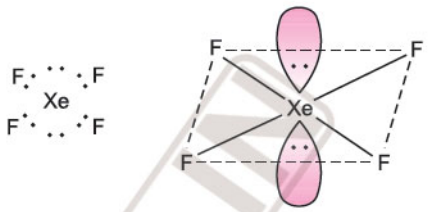
Fig. 18. Shape of BrF_5 molecule according to VSEPR theory.

The geometry of BrF_5 is termed as **square pyramidal.** IF_5 molecule has same geometry.

(*b*) Molecules containing 4bp and 2lp; AB_4L_2

Shape of XeF_4 (xenon tetrafluoride) molecule

In this case, the central xenon atom has eight electrons. In the formation of XeF_4, there are four bond pairs and two lone pairs. The six electron pairs has octahedral geometry (Fig. 19), in which two positions are occupied by lone pairs. The structure is termed as **square planar**.

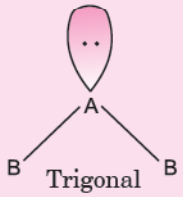
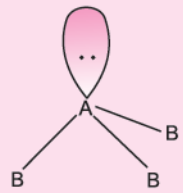
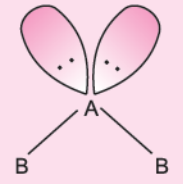
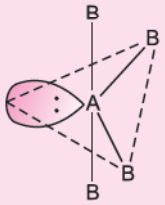


Square planar

Fig. 19. Shape of XeF_4 molecule according to VSEPR theory.

The shapes of some molecules according to VSEPR theory are summed up in Table 8.

Table 8. Shapes of some simple molecules or ions with central atom having one or more lone pairs of electrons.

Molecule type	No. of bonding pairs	No. of lone pairs	Total electron pairs	Arrangement of electron pairs	Shape (Geometry)	Example
AB_2L	2	1	3	 Trigonal planar	Bent or V shaped	SO_2, O_3, $SnCl_2$
AB_3L	3	1	4	 Tetrahedral	Pyramidal	NH_3
AB_2L_2	2	2	4	 Tetrahedral	V shaped	H_2O
AB_4L	4	1	5	 Trigonal bipyramidal	See saw	SF_4

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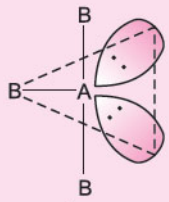
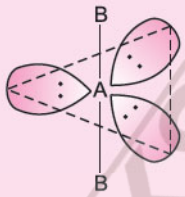
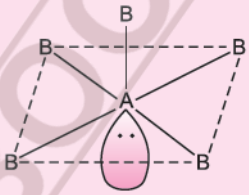
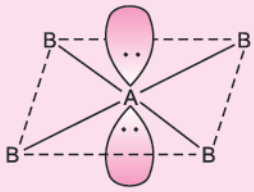
AB_3L_2	3	2	5	 Trigonal bipyramidal	T shaped	ClF_3
AB_2L_3	2	3	5	 Trigonal bipyramidal	Linear	XeF_2
AB_5L	5	1	6	 Octahedral	Square pyramidal	BrF_5
AB_4L_2	4	2	6	 Octahedral	Square planar	XeF_4

Practice Problems

15. Arrange the following sets of molecules in the decreasing order of bond angle :

(i) SF_6, CCl_4, H_2O, NH_3

(ii) CH_4, NH_3, H_2O, BF_3

(iii) $AlCl_3$, H_2S, BeH_2, H_2O

16. Out of the following data assign the correct bond angle associated with each of the given compounds.

Compounds	*Bond angles*
H_2O, CO_2, CCl_4, BF_3	180°, 109°28′, 104.5°,
BeF_2, $AlCl_3$, PF_5, SF_6	107°, 120°, 90°
NH_3, CH_4	

17. Give one example each of molecules which have the following geometries ;

(a) Linear *(b)* Trigonal bipyramidal

(c) Tetrahedral.

Answers to Practice Problems

15. *(i)* CCl_4, (109.5°), NH_3(107°), H_2O(104.5°), SF_6(90°)

(ii) BF_3, (120°), CH_4(109.5°), NH_3(107°), H_2O(104.5°)

(iii) BeH_2, (108°), $AlCl_3$(120°), H_2S(104.5°), H_2S(100°)

16. H_2O = 104.5°, CO_2 = 180°, CCl_5 = 109.5°, BF_3 = 120°

BeF_2 = 180°, $AlCl_3$ = 120° PF_5 = 120°, 90°, SF_6 = 90°

NH_3 = 107°, H_2O = 104.5°.

17. *(a)* BeF_2 *(b)* PF_5 *(c)* CH_4

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VALENCE BOND APPROACH OF COVALENT BOND

The simple concept of covalent bond formation as a result of sharing of electrons does not provide any clue for the forces operating between atoms. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in different molecules. For example, both H_2 and F_2 molecules have a single covalent bond formed by sharing of an electron pair between the respective atoms but they have quite different bond enthalpies and bond lengths as :

Molecule	H_2	F_2
Bond enthalpy	435.8 kJ mol^{-1}	150.6 kJ mol^{-1}
Bong length	74 *pm*	42 *pm*

The simple picture of covalent bonding also gives no idea about the shapes of polyatomic molecules. Similarly, the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also has limited applications.

To overcome these limitations, two important theories based on quantum mechanical principles are commonly used. These are:

1. Valence bond (VB) theory
2. Molecular orbital (MO) theory

Let us briefly learn about these two theories.

Valence Bond theory

The valence bond theory was put forward by Heitler and London in 1927. It was later improved and developed by L. Pauling and J. C. Slater in 1931. The valence bond theory is based on the knowledge of atomic orbitals and electronic configurations of elements, overlap criteria of atomic orbitals and stability of molecule.

The **basic assumptions** of this theory are :

(*i*) Atoms do not lose their identity even after the formation of the molecule.

(*ii*) The bond is formed due to the interaction of only the valence electrons as the two atoms come close to each other. The inner electrons do not participate in the bond formation.

(*iii*) During the formation of bond, only the valence electrons from each bonded atom lose their identity. The other electrons remain unaffected.

(*iv*) The stability of bond is accounted by the fact that the formation of bond is accompanied by release of energy. The molecule has minimum energy at a certain distance between the atoms known as **internuclear distance**. Larger the decrease in energy, stronger will be the bond formed.

To understand the concept more clearly, let us consider the formation of H_2 molecule.

Valence Bond Treatment for H_2 Molecule

Consider two hydrogen atoms A and B approaching each other having nuclei H_A and H_B and the corresponding electrons e_A and e_B respectively. When the two atoms are at large distances from each other, no interaction between the two atoms takes place. At this stage, the total energy of the system is the sum of the energies of the individual atoms. When the two atoms come closer, new attractive and repulsive forces begin to operate. Besides the attraction of the nucleus of one atom for its own electrons *i.e.* H_A–e_A and H_B–e_B, the following attractive and repulsive forces start operating :

(i) Attractive forces. Attractive forces operate between electron of atom A (e_A) and nucleus of B (H_B) and electron of atom B (e_B) and nucleus of A (H_A). These two new attractive forces are shown in Fig. 20 (*a*).

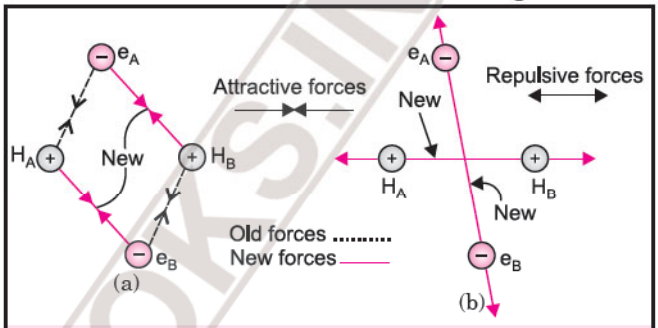

Fig. 20. (*a*) Attractive and (*b*) repulsive forces during formation of H_2 molecule.

***(ii)* Repulsive forces.** Repulsive forces are present between the nuclei H_A–H_B and electrons of two atoms e_A–e_B. These two forces are shown in Fig. 20 (*b*).

Thus, the forces operating in the molecule are :

Attractive :

(*i*) Nucleus of one atom and its own electron
$H_A - e_A$ and $H_B - e_B$

(*ii*) Nucleus of one atom and electron of other atom:
$H_A - e_B$ and $H_B - e_A$

Repulsive :

(*i*) Electrons of two atoms :
$e_A - e_B$

(*ii*) Nuclei of two atoms :
$H_A - H_B$

Now we know that attractive forces tend to bring the atoms closer while repulsive forces tend to push them apart. *It has been observed experimentally that the magnitude of the new attractive forces is more than the new repulsive forces.* As a result, the two atoms approach each other (Fig. 21) and the potential energy of the system decreases. This situation has been shown in Fig. 21 (*b*) where the two atoms are close together. As the two atoms come closer and closer, the system becomes more and more stable due to decrease of energy. Ultimately, a stage is reached where the total forces of attraction balance the forces of repulsion and the system acquires minimum energy. This is shown in Fig. 21 (*c*). At this stage, the two hydrogen atoms are said to be bonded together to form a stable molecule and the distance (r_0) between the atoms is known as **bond length**. For hydrogen molecule, the distance between two hydrogen atoms corresponding to minimum energy is 74 *pm*. The potential energy of the system when two atoms are brought closer and

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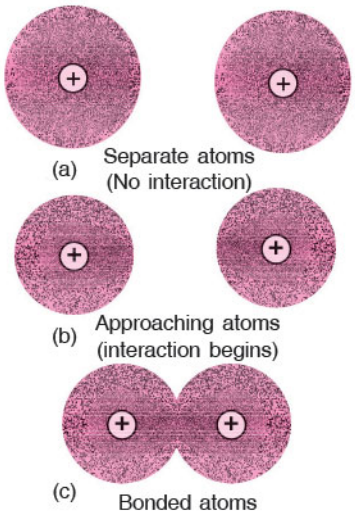

Fig. 21. Formation of hydrogen molecule when two hydrogen atoms approach each other.

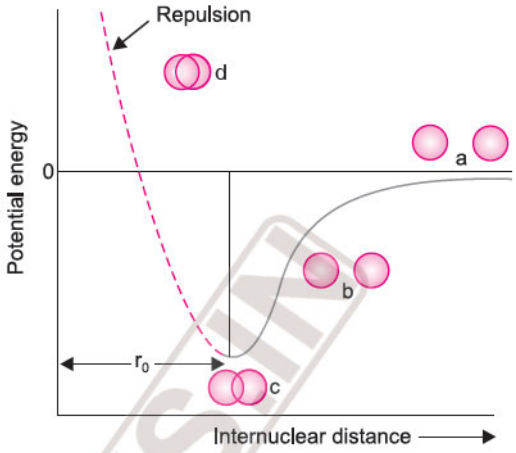

Fig. 22. Change of potential energy as two hydrogen atoms are brought closer and closer.

closer is represented in Fig. 22. This is called potential energy diagram. In this diagram, when the two atoms are for apart (stage *a*), there is no attractive or repulsive interactions between them and the potential energy of the system (isolated atoms) is assumed to be zero.

Thus, when the bond is formed, energy is released and therefore, the hydrogen molecule is more stable than the individual hydrogen atoms. That is,

$$H + H \longrightarrow H_2 + 435.8 \text{ kJ mol}^{-1}$$

This energy corresponding to minimum in the curve is called **bond energy.**

Conversely, when one mole of H_2 molecules is dissociated to hydrogen atoms, 435.8 kJ of energy is needed.

$$H_2\,(g) + 435.8 \text{ kJ mol}^{-1} \longrightarrow H\,(g) + H\,(g)$$

It may be remembered that the two hydrogen atoms cannot be brought closer than 74 pm* because then the repulsive forces will become large and the potential energy would rise [stage(*d*) shown by dotted line in Fig. 22].

Why is helium molecule, He_2 not formed ?

Now let us understand as to why He_2 molecule is not formed. This can be easily understood by calculating the attractive and repulsive forces when two helium atoms approach each other. Each helium atom has two electrons in its 1*s*-orbital. There are two attractive forces between the nucleus and the electrons of each atom.These are shown by dotted lines in Fig. 23 (*a*). It has been found that when two helium atoms approach each other, *four new attractive forces* and *five new repulsive forces* come into play. Therefore, repulsive forces predominate and the potential energy of the system increases which leads to unstability. Thus, He_2 represents unstable state and a chemical bond is not formed between helium atoms. Hence, He_2 molecule is not formed.

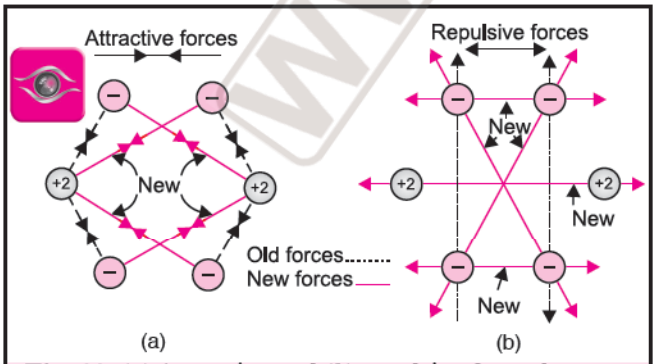

Fig. 23. (*a*) Attractive and (*b*) repulsive forces between helium atoms.

Orbital Overlap Concept of Covalent Bond

When two atoms approach each other, partial merger of two bonding orbitals, known as **overlapping of the orbitals** occurs. The overlapping of orbitals results in the pairing of electrons. The strength of a covalent bond depends upon the extent of overlapping. *The greater the overlapping, the stronger is the bond formed between two atoms.*

Let us explain the formation of a molecule of hydrogen by this method. A hydrogen atom has one electron in 1s-orbital. Now according to Pauli's exclusion principle, an orbital can hold two electrons of opposite spins. When these two atoms having electrons with opposite spins approach each other closely, their orbitals overlap (Fig. 24). Due to the overlapping, the two atomic orbitals merge into a bigger cloud called **molecular orbital.** The molecular orbital contains both the electrons. The two electrons can, therefore, be shared under these conditions. As a result, the two hydrogen atoms are held together in the form of a molecule. Thus, according to orbital theory, the formation of a covalent bond between two atoms results by pairing of electrons with opposite spins belonging to valence shells of two atoms.

*1 pm = 10^{-12} m, 74 pm = 74 × 10^{-12} m = 0.074 nm = 0.74 Å

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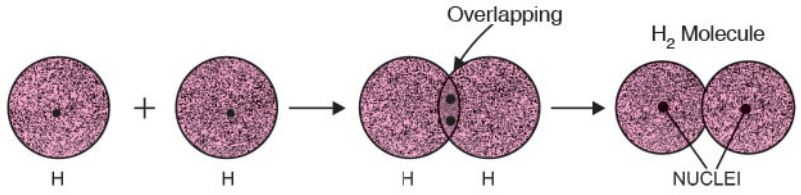


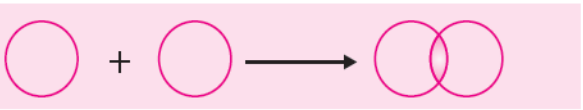
Fig. 24. Overlapping of orbitals of hydrogen atoms.

Types of Overlapping and Nature of Covalent Bonds

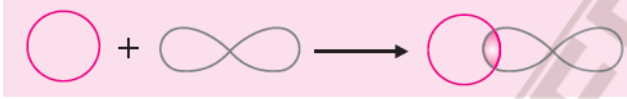
Depending upon the type of overlapping, the covalent bonds may be divided into two types : (a) *sigma* (σ) *bond* and (b) *Pi* (π) *bond*

***(a)* Sigma (σ) bond.** *This type of covalent bond is formed by the end to end hand on overlapping of bonding orbitals along the internuclear axis.* The overlap is known as **head on overlap or axial overlap.** The sigma bond is formed by any one of the following types of combinations of atomic orbitals :

***(i) s-s* overlapping.** In this type, two half-filled *s*-orbitals overlap along the internuclear axis as shown below:



(*ii*) ***s-p* overlapping.** This type of overlapping occurs between the half-filled *s*-orbital of one atom and half-filled *p*-orbital of the other atom.

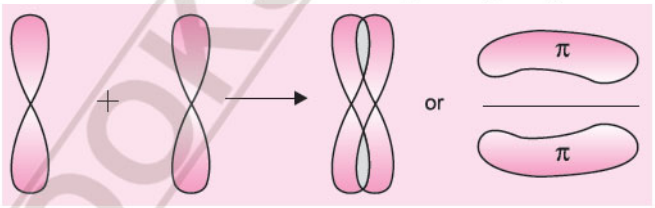


s-orbital *p*-orbital *s-p* overlap

(*iii*) ***p-p* overlapping.** This type of overlapping occurs between half-filled *p*-orbitals of the two approaching atoms.

p-orbital *p*-orbital *p-p* overlap

***(b) Pi* (π) bond.** *This type of covalent bond is formed by the sidewise overlap of the half-filled atomic orbitals of bonding atoms.* Such an overlap is known as **sidewise** or **lateral overlap.** The atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbital obtained as a result of sidewise overlap consists of two saucer type charged clouds above and below the plane of the participating atoms.



p-orbital *p*-orbital *p-p* overlap

Strength of sigma and *pi*-bonds. The strength of a covalent bond depends upon the extent of overlapping of atomic orbitals forming the bond. During the formation of a sigma bond, the overlapping of orbitals takes place to a larger extent. On the other hand, during the formation of a pi-bond, the overlapping occurs to a smaller extent. Therefore, *a sigma bond is stronger than a pi-bond.*

It is interesting to note that pi-bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules having multiple bonds (double or triple covalent bond).

Comparison of sigma and *pi*-bond. Sigma and *pi*-bonds differ in the following respects :

Table 9. Comparison of sigma and *pi*-bond.

Sigma (σ) Bond	pi(π)Bond
1. A sigma bond is formed by the end to end filled atomic orbitals along the internuclear axis. The overlapping involves two *s*-orbitals, one *s* and *p*-orbital or two *p*-orbitals.	A pi-bond is formed by the sidewise overlap of two half-filled *p*-orbitals.
2. In this case, the overlapping can take place to a larger extent and therefore, the bond formed is a strong bond.	In the formation of π-bond the overlapping occurs to a lesser extent and therefore, the bond is weak.
3. The molecular orbital is symmetrical about the internuclear axis.	The molecular orbital is discontinuous and consists of two charged clouds above and below the plane of atoms.
4. There can be free rotation of atoms around the σ-bond.	Because of overlapping of the electron clouds above and below the plane of the atoms, free rotation of atoms around π-bond is not possible.
5. The bond may be present between two atoms either alone or along with π-bond.	The bond is always present between two atoms in addition to sigma bond.
6. In the formation of sigma bond, *s*-orbitals can participate.	*s*-orbitals cannot participate in the formation of *pi*-bond

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DIRECTIONAL PROPERTIES OF COVALENT BONDS

As we have learnt the formation of covalent bond depends largely on the overlap of atomic orbitals between atoms. The formation of a hydrogen (H_2) molecule is essentially due to the overlap of the 1*s* orbitals of two H atoms when they combine with each other. In general, **the greater the extent of overlapping, the stronger is the bond formed.**

In the case of polyatomic molecules like CH_4, NH_3 and H_2O, in addition to formation of bonds, the geometry (shape) of the molecules is also important. For example, why is CH_4 molecule tetrahedral in shape and HCH bond angles are 109°28′. Why is NH_3 molecule pyramidal in shape ?

The valence bond theory explains the formation and the directional properties of bonds in polyatomic molecules in terms of overlap of atomic orbitals and a new concept known as hybridisation of atomic orbitals.

Overlap of Atomic Orbitals

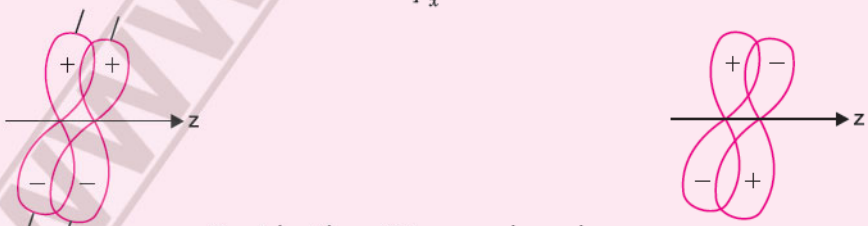
When the two atoms approach each other, their atomic orbitals overlap. The overlap between different types of *s* and *p* orbitals can be positive, negative or zero depending upon the properties of the overlapping atomic orbitals. For example, when two $2p_z$ orbitals overlap along the internuclear axis with the lobes of same sign, then positive overlapping occurs. On the other hand, when these two $2p_z$ orbitals overlap along the internuclear axis with the lobes of opposite sign, negative overlap occurs because lobes of opposite sign cannot combine. Similarly, the different arrangements of *s*- and *p*-orbitals overlap resulting in positive, negative and zero overlaps are shown below :

Positive overlap **Negative overlap**

Combination of $2p_z$ atomic orbitals

Combination of $2p_z$ and $2s$ atomic orbitals

Combination of $2p_x$ atomic orbitals



Combination of $2p_y$ atomic orbitals

Zero overlap

Combination of $2s$ and $2p_x$ atomic orbitals

Combination of $2p_x$ and $2p_y$ atomic orbitals

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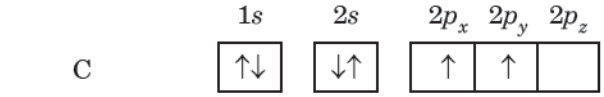
HYBRIDISATION

In order to explain the characteristic geometrical shapes of polyatomic molecules, Pauling introduced the concept of hybridisation.

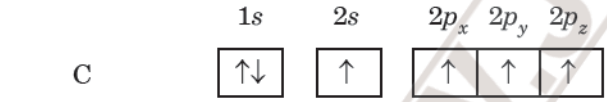
To understand this, let us consider a simple molecule, methane (CH_4). The ground state electronic configuration of carbon is $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$. This may be represented as :



(Ground state)

There are only two half-filled orbitals in the valence shell of carbon. Therefore, its bonding capacity should be two. Carbon is expected to form compounds like CH_2, CCl_2, etc. However, in actual practice, carbon exhibits the bonding capacity of four and is known to form molecules such as CH_4, CCl_4, etc.

This can be explained on the basis of **promotion concept.** In order to explain the bonding capacity of carbon, it was proposed that one of the electrons from 2*s*-filled orbital is promoted to the 2*p*-empty orbital ($2p_z$), which is in a higher energy state. Thus, four half-filled orbitals are formed in valence shell which account for the bonding capacity of four bonds of carbon. This state is known as **excited state** and the process is called **promotion***. Thus, four half filled orbitals get formed in the valence shell which account for the bonding capacity of four of carbon. The electronic configuration of carbon in the excited state is :



(Excited state)

Now the four orbitals of carbon with one unpaired electron can overlap with the 1*s* orbitals of the four H atoms which are also singly filled. This will result in the formation of C–H bonds. However, all the four bonds formed by carbon will not be equivalent. For example, in the formation of CH_4 molecule, one C—H bond will be formed by overlaping of 2*s*- orbital of C and 1*s*- orbital of H whereas the other three C—H bonds will be formed by the overlapping of 2*p*- orbital of C and 1*s*- orbital of H. But in methane (CH_4), all the four bonds of carbon are equivalent. The equivalent character of the bonds can be explained with the help of a new concept known as **hybridisation of atomic orbitals** which was introduced by Pauling. This is an important aspect of Valence Bond Theory.

According to Pauling, the atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals. Instead of pure atomic orbitals, these hybrid orbitals are used in bond formation. This process is known as **hybridisation.** This may be defined as :

the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies resulting in the formation of new set of orbitals of equivalent energies and shape.

The new orbitals formed as a result of hybridisation are called **hybrid** or **hybridised orbitals**. Thus, to form four equivalent bonds, *one* 2*s* and *three* 2*p*-orbitals of carbon hybridise and form four new orbitals called ***sp*³ (pronounced as *s–p*³) hybrid orbitals**.

Characteristics of Hybridisation

1. The number of hybridised orbitals formed is equal to the number of the orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. The hybrid orbitals are directed in space in some preferred directions to have stable arrangement. Therefore, the type of hybridisation indicates the **geometry of the molecule.**

Conditions for Hybridisation

(*i*) Only the orbitals present in the valence shell of the atom are hybridised.

(*ii*) The orbitals undergoing hybridisation should have only a small difference in energy. The orbitals which differ largely in energy cannot take part in hybridisation.

(*iii*) Promotion is not essential condition prior to hybridisation.

*The promotion of electrons from 2*s* to 2*p* orbital of higher energy level will require an input of energy. From where this energy comes? We know that the formation of covalent bonds is accompained by release of energy. Thus, when reacting atoms say H atoms approach a carbon atom to form covalent bonds, energy is released. This energy released is used to promote one electron from 2*s* to 2*p* orbital.

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(*iv*) It is not essential that only half filled orbitals participate in hybridisation. In certain cases, even filled orbitals of valence shell participate in hybridisation.

There are many types of hybridisation involving different atomic orbitals. In the present unit, we shall discuss only the various types of hybridisation involving *s*, *p* and *d*-orbitals. The different types of hybridisations are discussed below :

1. *sp*-Hybridisation.

In *sp* hybridisation, one *s*- and one *p*-orbitals mix and form two equivalent *sp* hybrid orbitals. The orbitals suitable for *sp* hybridisation are *s* and p_z orbitals, if the hybrid orbitals are to lie along Z–axis. The *sp* hybridisation is pictorially shown below :

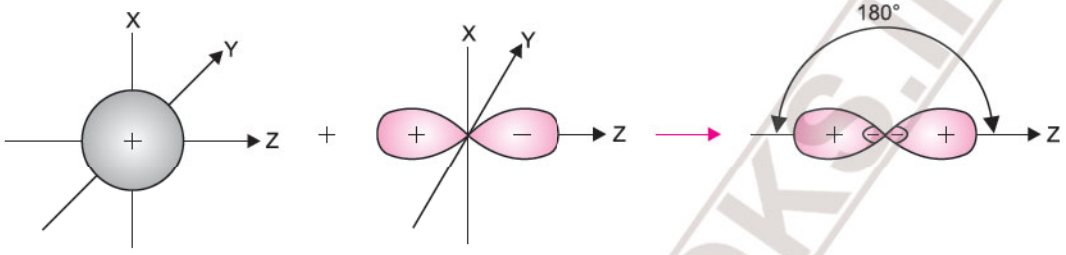

Fig. 25. Formation of *sp* hybrid orbitals.

Each *sp* hybrid orbital has 50% *s*-character and 50% *p*–character. These two *sp* hybrid orbitals point in opposite directions along the Z-axis with bigger positive lobes and very small negative lobes. This provides for more effective overlap resulting in the formation of stronger bonds. These two *sp* hybrid orbitals lie along **linear arrangement** and therefore, it is also called **linear hybridisation.**

The formation of linear molecules like $BeCl_2$, BeF_2, BeH_2 can readily be explained.

Shape of BeF_2 molecule. The electronic configuration of beryllium is $1s^2\ 2s^2$. To account for divalency of Be, one of the 2*s*-electrons is promoted to the vacant 2*p*-orbital. These two orbitals (2*s* and 2*p*) get hybridised to form two *sp* hybrid orbitals. These two *sp* hybrid orbitals are oriented in a linear arrangement. Each of these overlaps with 2*p*-orbital of fluorine to form two Be—F bonds. Thus, BeF_2 is **linear** and bond angle is 180°. This is shown below :

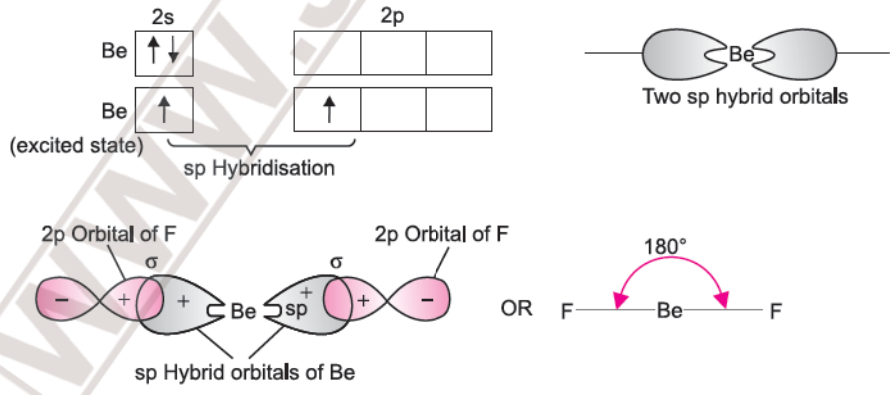

Fig. 26. Formation of BeF_2 molecule.

2. sp^2-Hybridisation.

In sp^2 hybridisation, one *s* and two *p*-orbitals hybridise to form three equivalent sp^2 hybrid orbitals. Each sp^2 hybrid orbital has one third (33.3%) *s*–character and two-third (66.7%) *p*–character. These three sp^2 hybrids orbitals remain in the same plane making an angle of 120° with one onother as shown in Fig. 27. This arrangement is also called **trigonal planar** arrangement and therefore, the molecules involving sp^2 hybridisation of the central atom will adopt **trigonal planar geometry**.

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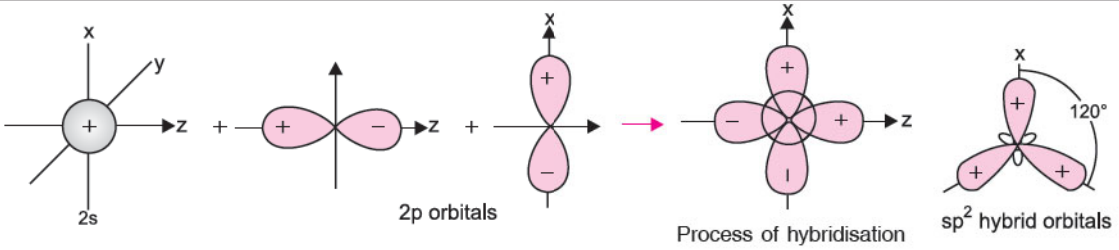

Fig. 27. Formation of three sp^2 hybrid orbitals.

This can be illustrated by considering the example of BCl_3 molecule.

Shape of BCl_3 molecule. In BCl_3, the central boron atom has $1s^2\ 2s^2\ 2p^1$ electronic configuration. To account for trivalency of B, one of the 2*s*–electrons is promoted to vacant 2*p*-orbital. Therefore, the excited state of boron has three unpaired electrons. These three orbitals (one 2*s* and two 2*p*) hybridise to form three sp^2 hybrid orbitals. These three hybrid orbitals are oriented in a trigonal planar arrangement. Each of these sp^2 hybrid orbitals overlaps with 2*p*-orbital of chlorine to form three B—Cl bonds. Thus, BCl_3 has **trigonal planar geometry** and ClBCl bond angle is 120°.

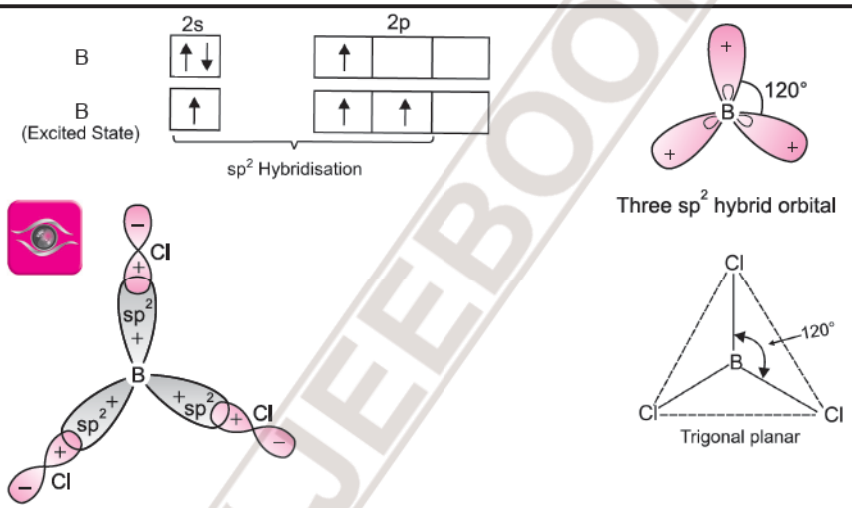

Fig. 28. Formation of BCl_3 molecule.

3. sp^3-Hybridisation.

In sp^3 hybridisation, one *s* and three *p*–orbitals hybridise to form four sp^3 hybrid orbitals. The four sp^3

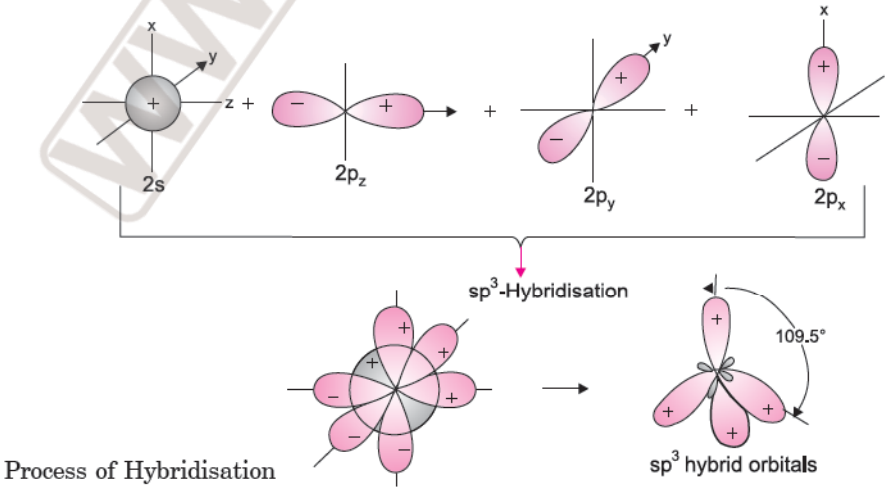

Fig. 29. Formation of four sp^3 hybrid orbitals.

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hybrid orbitals will be directed towards the four corners of a regular tetrahedron and make an angle of 109° 28′ (or 109.5°) as shown in Fig. 29. Each sp^3 hybrid orbital has one fourth (25%) *s*–character and three–fourth (75%) *p*–character.

This can be illustrated by taking the example of methane (CH_4) molecule.

Formation of methane (CH_4). The central atom carbon has the ground state electronic configuration as $1s^2 2s^2 2p_x^1 2p_y^1$. It has only two unpaired electrons. To account for tetravalency, one of the 2*s*–electrons is promoted to vacant 2*p*-orbital. Therefore, the excited state of carbon has four unpaired electrons. These four orbitals (one 2*s* and three 2*p*) hybridise to form four sp^3 hybrid orbitals, which are oriented in tetrahedral arrangement. Each of these sp^3 hybrid orbital overlaps with 1*s* orbital of hydrogen to form four C – H bonds. Thus, methane molecule has **tetrahedral** geometry with each HCH bond angle of 109.5° as shown in Fig. 30.

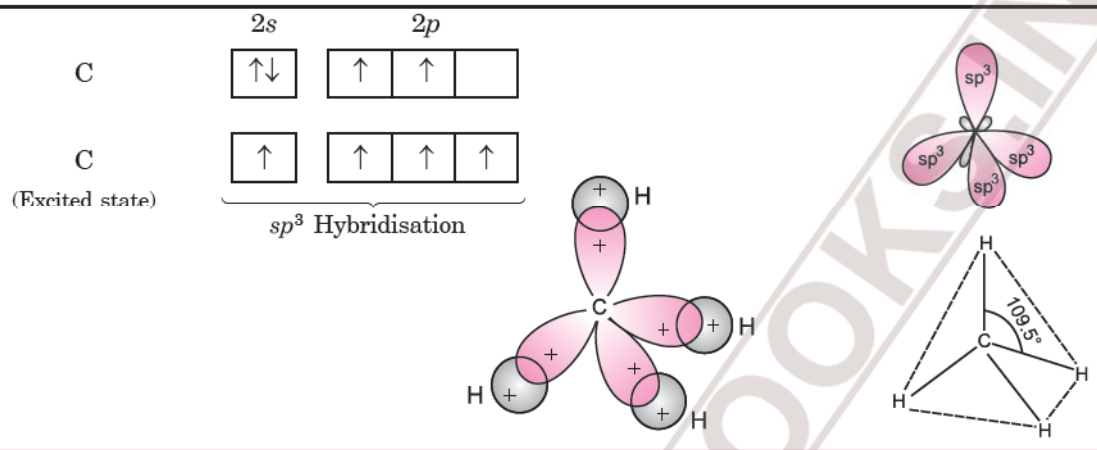

Fig. 30. Formation of CH_4 molecule.

The structures of NH_3 and H_2O can also be explained on the basis of sp^3 hybridisation of N and O bonds in these molecules as explained below :

Ammonia molecule (NH_3). The ground state electronic configuration of nitrogen atom is : $1s^2\ 2s^2\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$. It contains three unpaired electrons in its ground state. Since nitrogen forms only three covalent bonds, there is no need of promotion. These four orbitals (2*s*, $2p_x$, $2p_y$ and $2p_z$) are hybridised to form four sp^3 hybrid orbitals. These four sp^3 hybrid orbitals adopt tetrahedral arrangement. One of these hybrid orbitals contains a lone pair of electrons while the remaining three contain one unpaired electron each. These three hybrid orbitals overlap with 1*s*-orbitals of hydrogen atoms to form three N—H sigma bonds.

Thus, in ammonia, the central atom N, is surrounded by three bond pairs (N—H bonds) and one lone pair of electrons.

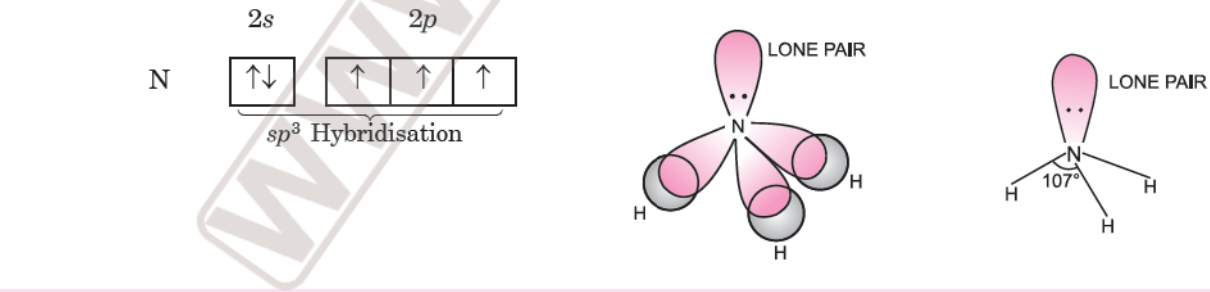

Fig. 31. Formation of ammonia molecule.

We know that the *force of repulsion between a lone pair and a bond pair is greater than the force of repulsion between two bond pairs of electrons*. The molecule, therefore, gets a little distorted and the bond angle H—N—H decreases from 109.5° to 107°. The shape of the molecule is thus **pyramidal** in which the nitrogen atom lies at the centre, three hydrogens form the base and the lone pair of electrons forms the apex of the pyramid.

Water molecule (H_2O). The ground state electronic configuration of the central oxygen atom is : $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$ and is represented in Fig. 32.

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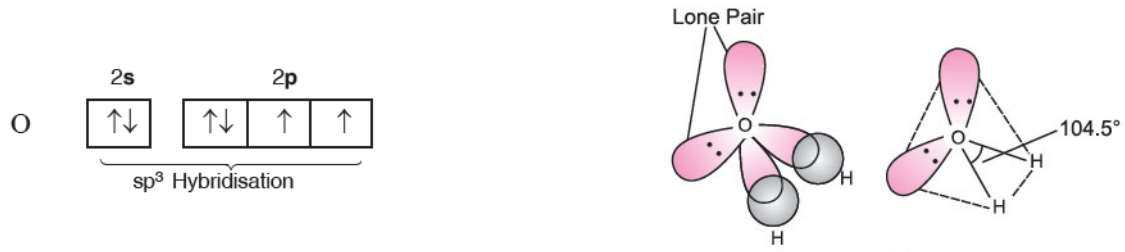

Fig. 32. Formation of water molecule involving sp^3 hybridisation.

Thus, there are two unpaired electrons which can form two bonds with hydrogen atoms, without involving any excitation of the oxygen atom. These four orbitals ($2s$, $2p_x$, $2p_y$ and $2p_z$) *undergo hybridisation to give four sp^3 hybrid orbitals of equivalent energy*. These four sp^3 hybrid orbitals adopt a **tetrahedral structure** with two corners occupied by hydrogen atoms and two corners occupied by lone pairs of electrons as shown in the figure.

Now, we known that the force of repulsion between the two lone pairs of electrons amongst themselves is more than the force of repulsion between a lone pair and a bond pair, which in turn is more than the force of repulsion between two bond pairs of electrons. Therefore, there is greater distortion in this molecule than in ammonia. Consequently, the bond angle HOH in water is even smaller than the bond angle HNH in ammonia. This has been found to be 104.5°. Such a structure is described as **V–shaped** or **angular.**

Unique property of carbon

Carbon has unique property that it can make use of three main types of hybridisations namely sp^3, sp^2 and sp under different conditions. These are discussed below :

1. sp^3 hybridisation of carbon.

As discussed earlier, carbon involves sp^3 hybridisation in methane, CH_4 molecule. Similarly, in ethane C_2H_6, carbon involves sp^3 hybridisation as discussed below :

Formation of ethane. In ethane ($H_3C—CH_3$) molecule, each carbon atom undergoes sp^3 hybridisation. One of the four sp^3 hybrid orbitals of one carbon atom overlaps axially with similar orbital of the other carbon atom to form C—C sigma bond. The remaining three hybrid orbitals belonging to both the carbon atoms overlap axially with the half-filled orbitals of hydrogen atoms to form C—H sigma bonds as shown in Fig. 33.

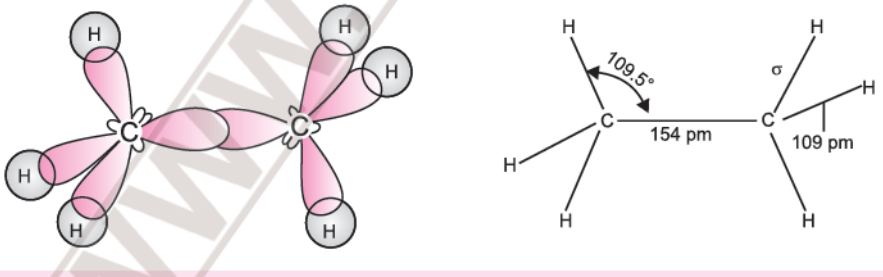

Fig. 33. Orbital picture of ethane.

Thus, in ethane, C—C bond length is 154 *pm* and each C—H bond length is 109 *pm*.

2. sp^2-hybridisation of carbon.

In this type, one s ($2s$) and two p-orbitals ($2p_x$, $2p_y$) present in the valence shell of the excited carbon atom get hybridised to form three equivalent orbitals called **sp^2 hybrid orbitals**.

The orbitals formed are directed towards the three corners of an equilateral triangle with the carbon atom in the centre. The hybridisation is, therefore, known as **trigonal hybridisation**.

Each sp^2 hybrid orbital has one-third s-character and two third p-character. The bond angle between the two hybridised orbitals is 120°. The unhybridised $2p_z$ orbital of carbon is oriented in a plane at right angles to the plane containing three hybridised orbitals as shown dotted in Fig. 34.

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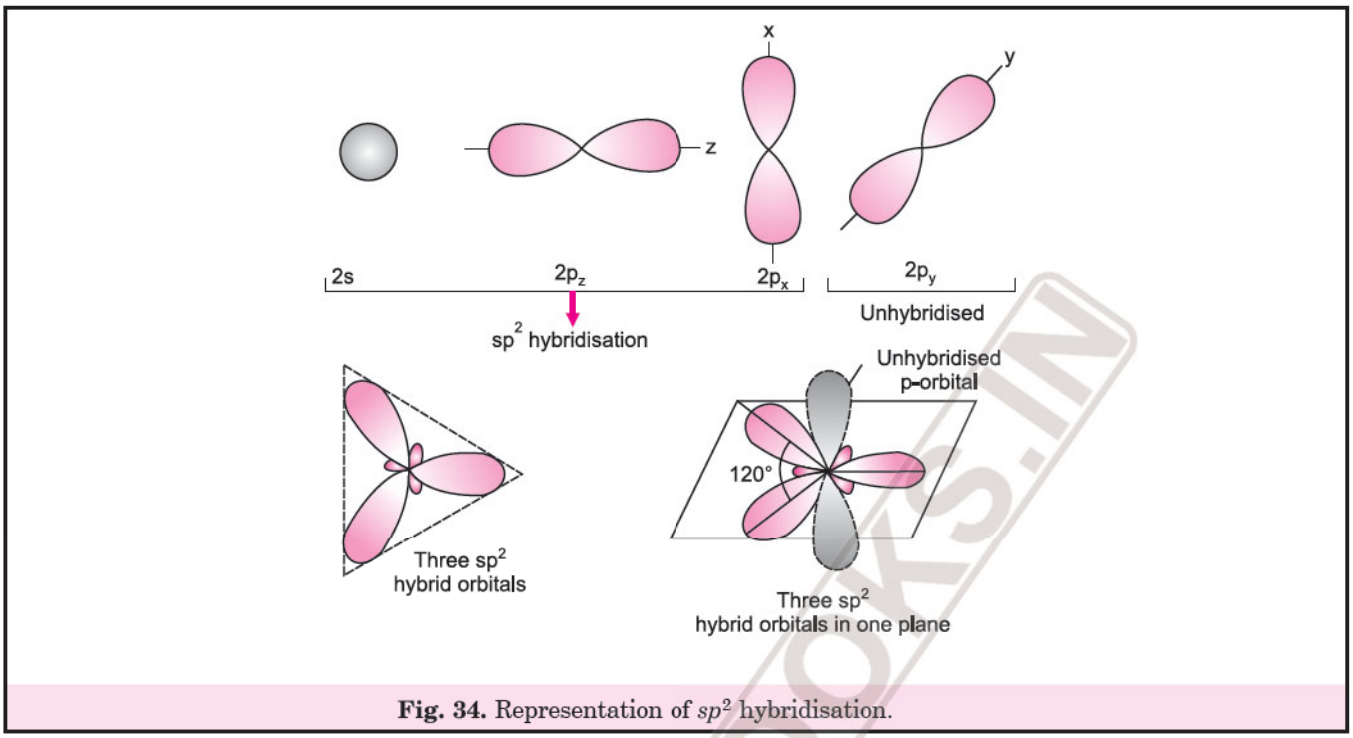
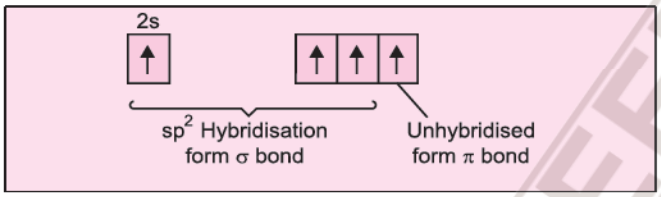


Fig. 34. Representation of sp^2 hybridisation.

Example. Let us illustrate sp^2 hybridisation with the help of ethylene or ethene ($H_2C = CH_2$) molecule.



Carbon atom has four unpaired electrons in the valence shell in the excited state. In the formation of ethylene, each carbon atom undergoes sp^2 hybridisation leaving $2p_z$ orbital unhybridised. One sp^2 hybridised orbital of one carbon atom overlaps axially with sp^2 hybridised orbital of the other carbon atom to form a stable sigma C—C bond. The remaining two sp^2 hybrid orbitals of both carbon atoms overlap axially with the half-filled 1*s*-orbitals of hydrogen atoms forming four C—H sigma (σ) bonds.

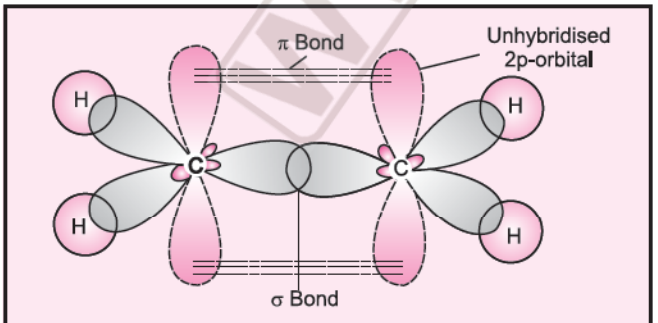


Fig. 35. Orbital picture of ethene.

The unhybridised orbital ($2p_z$) of one carbon atom overlaps sidewise with the similar orbital of the other carbon atom to form weak pi (π) bond. The π-bond consists of two equal electron clouds distributed above and below the plane of other atoms. Thus, in ethylene all the six atoms (forming σ-bonds) lie in one plane and π-bond is at a plane perpendicular to the plane of six atoms (Fig. 36).

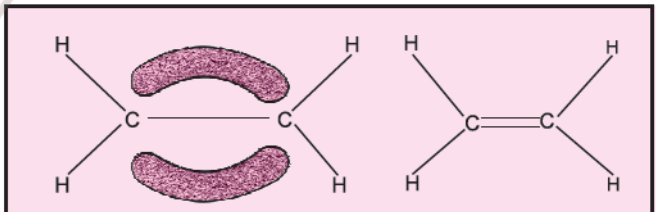


Fig. 36. Electron cloud picture of ethene.

Since there is an equal probability of locating the electron density in both the lobes of the p-orbitals, the same π-bond is formed above and below the internuclear axis representing σ-bond. As pointed out earlier, π-bond is weaker than the σ-bond since the electrons involved are more diffused in space in the molecular form of a cloud. The presence of such a bond in ethene makes it highly reactive in nature. It is, therefore, regarded as *unsaturated* molecule. In ethene molecule,

C=C bond length = 134 pm,
C—H bond length = 108 pm.
H—C—H bond angle = 117.6°,
H—C—C bond angle = 121°.

3. *sp* hybridisation of carbon

In *sp* hybridisation, one *s* (2*s*) and one *p* ($2p_x$) orbitals present in the valence shell of the excited

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carbon atom get hybridised to form two equivalent orbitals while the remaining two 2*p*-orbitals ($2p_y$ and $2p_z$) do not take part in hybridisation. The entire phenomenon of the electron promotion followed by hybridisation has been shown in Fig. 37. Due to mutual repulsion of the electron clouds, the two hybridised orbitals are inclined to each other at an angle of 180°. The hybridisation is often known as *diagonal hybridisation* and has been represented in Fig. 37. Each *sp* hybrid orbital has equal *s*-and *p*-character, *i.e.*, one-half *s*- and one-half *p*-character.

The two unhybridised orbitals are directed along *y*-axis and *z*-axis while the two hybridised orbitals are directed towards the third axis (*x*-axis).

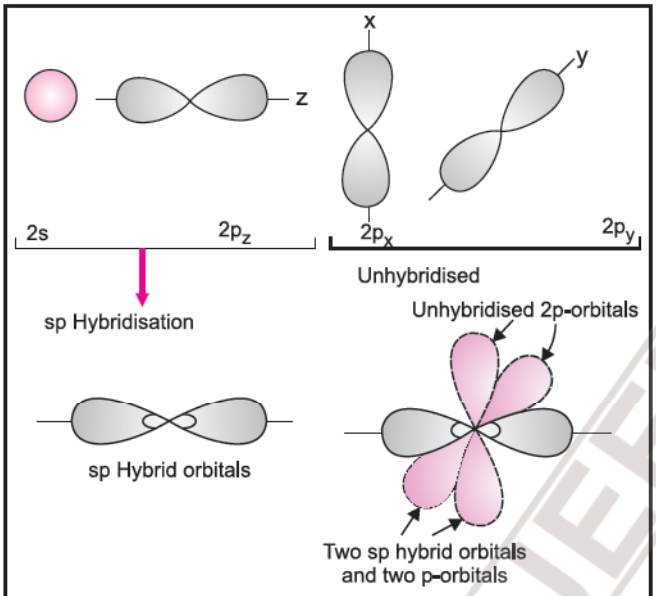

Fig. 37. Representation of *sp* hybridisation.

Example. *sp* type or *diagonal* hybridisation can be illustrated with the help of acetylene or ethyne (HC ≡ CH) molecule.

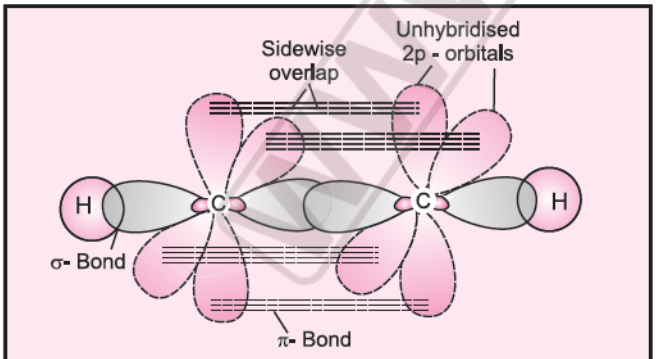

Fig. 38. Orbital picture of ethyne.

In the formation of ethyne, both the carbon atoms undergo *sp*-hybridisation leaving two unhybridised orbitals ($2p_y$ and $2p_z$) on each. One *sp* hybrid orbital of one carbon atom overlaps axially with *sp* hybrid orbital of the other carbon atom to form C—C sigma (σ) bond. The remaining hybridised orbital of each carbon atom overlaps axially with half-filled orbital of hydrogen forming σ-bonds. Each of the two unhybridised orbitals of one carbon atom overlaps sidewise with the similar orbitals of the other carbon atom to form two π-bonds.

So, the triple bond between two carbon atoms is made up of one sigma and two pi bonds. If one π–cloud is pictured as lying above and below the internuclear axis representing σ– bond then the other π-cloud lies in front and in back as shown in Fig. 39 (*a*). However, there is over lapping between the π–cloud so that the four lobes of two π–bonds merge to form a single cylindrical electron cloud about the internuclear axis as shown in Fig. 39. (*b*) Thus in acetylene molecule:

C≡C bond length = 120 pm
C–H bond length = 106 pm
H–C–C bond angle = 180°

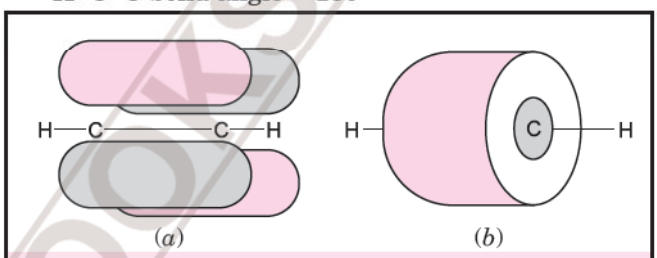

Fig. 39. Ethyne molecule sharing two π-bonds.

Hybridisation in Elements Involving *d*-orbitals

The elements of third period contain *d*-orbitals also in addition to *s*- and *p*-orbitals. The 3*d*-orbitals are comparable in energy to the 3*s*- and 3*p*-orbitals. These *d*-orbitals are also involved in the hybridisation to explain the geometries of molecules of elements of third period. This results in covalencies of 5, 6 and 7, which are not known amongst the compounds of second period elements. Due to the availability of *d*-orbitals, P and S can exhibit covalency of 5 and 6 respectively whereas the corresponding elements of same group N and O of second period cannot extend their octets.

For example, in the ground state phosphorus and sulphur have three and two half filled orbitals (like nitrogen and oxygen) respectively. Thus, they form compounds like PF_3 and H_2S. But P and S also form hypervalent compounds like PF_5 and SF_6. However, N and O cannot form corresponding SF_6 and OF_6 molecules. This is a **feature of elements of third period** in which they can extend their octets.

Let us understand some common types of hybridisations involving *d*-orbitals and common examples of molecules of third period.

1. sp^3d-hybridisation

This hybridisation involves the mixing of one *s*, three *p* and one *d*-orbitals. These five orbitals hybridise to form five sp^3d-hybrid orbitals. The mixing of five orbitals is shown in Fig. 40. These hybrid orbitals point towards the corners of a *trigonal bipyramidal geometry*. In this case, the three orbitals forming a plane are directed towards the corners of an equilateral triangle while the other two are perpendicular to the plane of the triangle lying above and below it.

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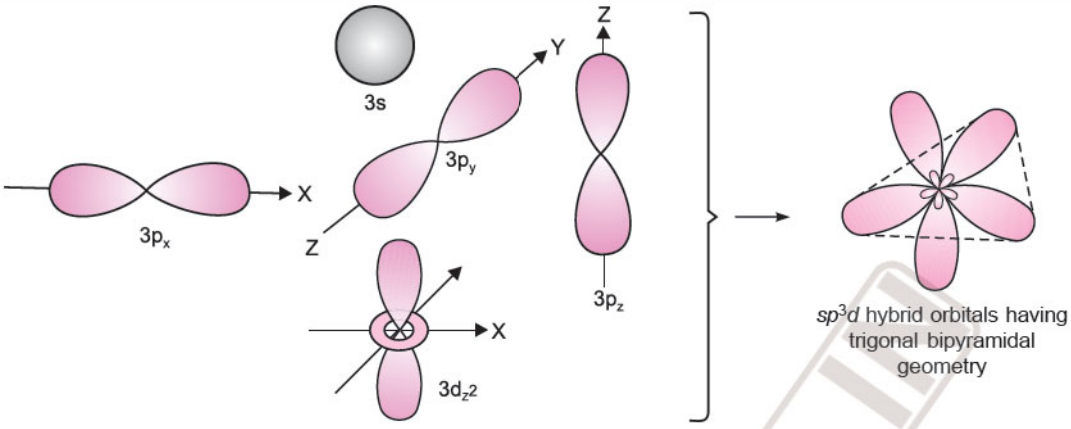

Fig. 40. Formation of five sp^3d hybrid orbitals which adopt trigonal bipyramidal geometry.

Phosphorus pentachloride involves sp^3d hybridisation as described below :

Geometry of PCl_5 molecule. The outer electronic configuration of phosphorus, (Z=15), the central atom, is $3s^2\ 3p^3$ which may be represented as shown in Fig. 41 (*a*). It has three unpaired electrons in the ground state.

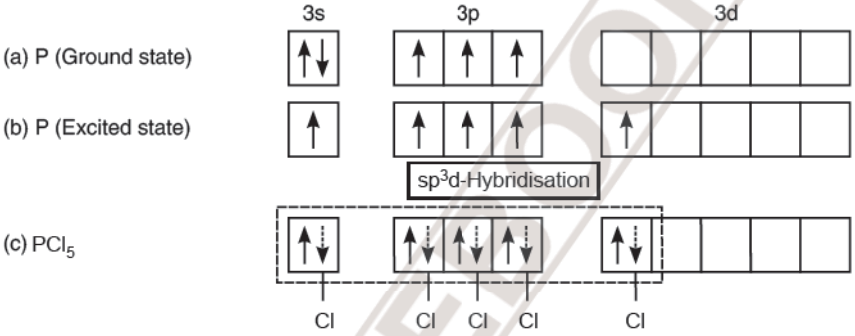

Fig. 41. Formation of PCl_5 molecule involving sp^3d hybridisation.

To explain the pentavalency of phosphorus in PCl_5, one of the electrons in 3*s*-orbital is promoted to the higher 3*d*-orbital so that it has five unpaired electrons. This is called the excited state of phosphorus and is represented in Fig. 41 (*b*). These five orbitals hybridise to form five sp^3d-hybrid orbitals which adopt trigonal bipyramidal arrangement. Each of the sp^3d-hybrid orbital overlaps with 3*p*-orbital of chlorine forming five P—Cl bonds as shown in Fig. 42.

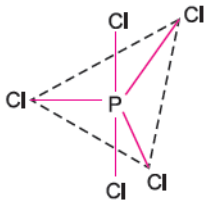

Fig. 42. Structure of PCl_5 molecule.

Thus, PCl_5 molecule has ***trigonal bipyramidal geometry.*** It may be noted that all the bond angles in trigonal bipyramidal geometry are not equivalent. Three bonds lie in one plane at an angle of 120° to one another as in a triangular planar arrangement. These bonds are termed as *equatorial bonds.* Of the remaining two bonds, one lies above and the other below the equatorial plane both making an angle of 90° with the plane. These bonds are called *axial bonds.* It may be remembered that this geometry is not symmetrical. *The axial bonds have been found to be larger than equatorial bonds.* For example, in case of PCl_5 molecule

each P — Cl axial bond = 219 pm

and each P — Cl equatorial bond = 204 pm

The larger bond length of axial bond in comparison to equatorial bond is because of greater repulsion from other bonds in axial position, (already discussed in VSPER theory). Therefore, the axial bonds are slightly larger and hence slightly weaker than equatorial bonds. Therefore, PCl_5 is quite reactive.

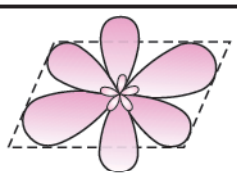

Fig. 43. Six sp^3d^2 hybrid orbitals which adopt octahedral geometry.

PF_5 also have similar hybridisation and geometry.

2. sp^3d^2-hybridisation.

In this case, one *s*, three *p* and two *d*-orbitals get hybridised to form six sp^3d^2-hybrid orbitals which adopt octahedral arrangement as given in Fig. 43.

Geometry of SF_6 molecule. The geometry of SF_6 molecule can be explained on the basis of sp^3d^2 hybridisation. In SF_6, the central sulphur atom has the ground state configuration, $3s^23p^4$ as shown in Fig. 44. To account for the

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hexavalency in SF_6, one electron each from $3s$ and $3p_x$ orbitals is promoted to $3d$-orbitals as shown in Fig. 44 (a). These six orbitals get hybridised to form six sp^3d^2-hybrid orbitals. Each of these sp^3d^2-hybrid orbitals overlaps with $2p$-orbital of fluorine to form S—F bond. Thus, SF_6 molecule has octahedral structure as shown in Fig. 44(b). The dotted electrons represent electrons from F-atoms.

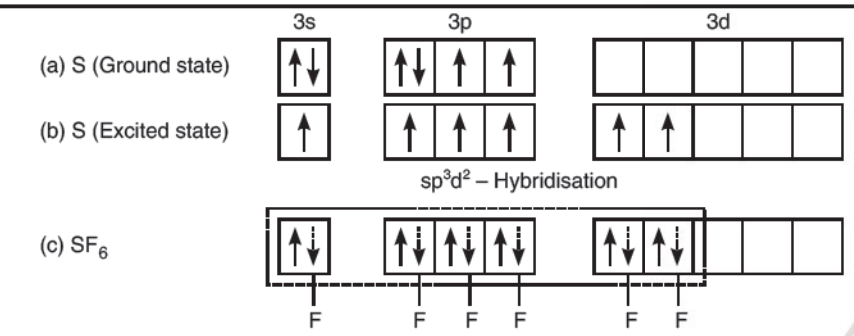


Fig. 44(a). Formation of SF_6 molecule involving sp^3d^2-hybridisation

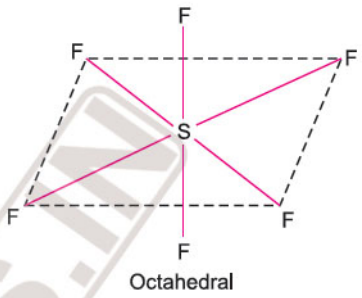


Fig. 44(b). Octahedral geometry of SF_6 molecule.

3. sp^3d^3-hybridisation.

This involves the mixing of one s, three p and three d-orbitals forming seven sp^3d^3-hybrid orbitals having **pentagonal bipyramidal geometry.** The geometry of IF_7 molecule can be explained on the basis of sp^3d^3-hybridisation.

Geometry of IF_7 molecule.

The outer electronic configuration of iodine atom is $5s^25p^5$. To make seven bonds, one s and two p-orbitals are promoted to the higher vacant $5d$-orbitals as shown in Fig. 45 (a) and (b). These seven orbitals are then hybridised to give seven sp^3d^3-hybrid orbitals. Each of these sp^3d^3-hybrid orbitals overlaps with $2p$-orbitals of fluorine to form IF_7 molecule having **pentagonal bipyramidal geometry.**

In this geometry, all the bond angles are not equal. Five F-atoms are directed towards the vertices of a regular pentagon making an angle of 72°. The other two F-atoms are at right angles (90°) to the plane. Due to different bond angles, the bonds are different in length. The axial bonds are larger than equatorial bonds.

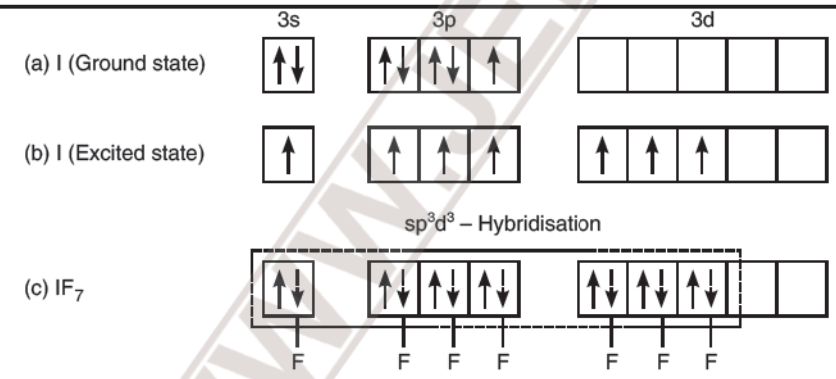


Fig. 45(a). Formation of IF_7 molecule involving sp^3d^3-hybridisation

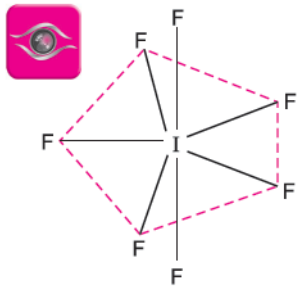
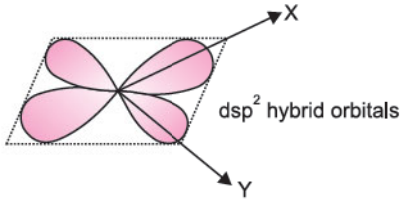


Fig. 45(b). Pentagonal bipyramidal geometry of IF_7 molecule.

4. dsp^2-hybridisation.

In addition to above types of hybridisations, dsp^2 type hybridisation is also known particularly for transition metal ions. The orbitals involved in this type of hybridisation are $d_{x^2-y^2}$, s and two p. The four orbitals hybridise to give square planar geometry as shown below :



Square planar arrangement

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The common example of a molecule involving dsp^2 hybridisation is $[Ni(CN)_4]^{2-}$.

Geometry of $[Ni(CN)_4]^{2-}$ ion. In this case, the oxidation state of nickel is +2. The ground state electronic configuration of nickel is $3d^8 4s^2$. Therefore, the electronic configuration of Ni^{2+} is $3d^8$. When the four CN^- ions come closer to Ni^{2+} ions, the two unpaired d–electrons are paired up thereby making a $3d$–orbital empty. These empty four orbitals (one $3d$, one $4s$ and two $4p$) hybrdise to form four dsp^2 hybrid orbitals. Each one of the four CN^- groups donates a lone pair of electrons to the vacant dsp^2 hybrid orbitals as shown

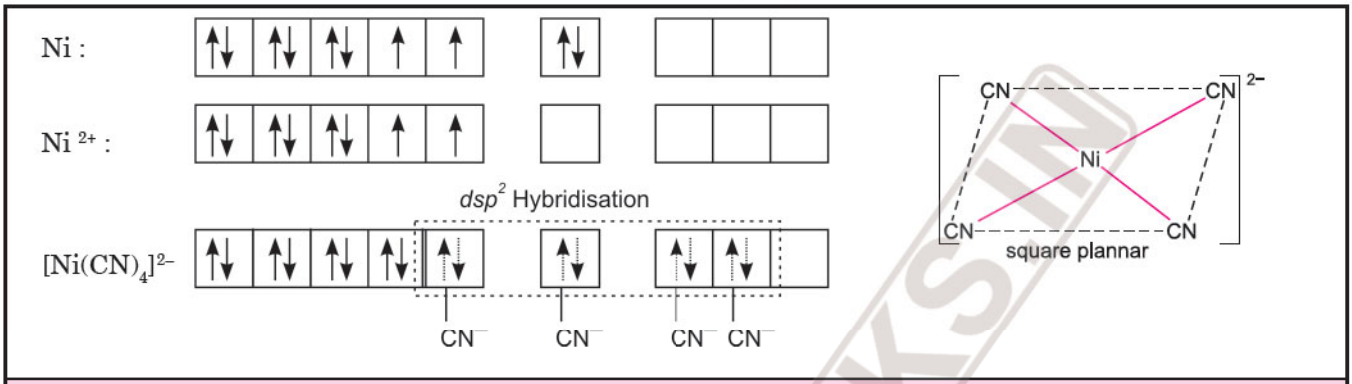


Fig. 46. Formation of $[Ni(CN)_4]^{2-}$ involving dsp^2 hybridisation of nickel. The dotted electrons are supplied by CN^- ions.

Thus, $[Ni(CN)_4]^{2-}$ has square planar geometry. It may be noted that in this case, the vacant orbitals are hybridised. The CN^- groups donate pair of electrons in these hybridised vacant orbitals.

REMEMBER

The d-orbitals used in different types of hybridisations

- sp^3d : d_{z^2}
- sp^3d^2 : $d_{x^2-y^2}$, d_{z^2}
- sp^3d^3 : d_{xy}, d_{yz}, d_{zx}
- dsp^2 : $d_{x^2-y^2}$

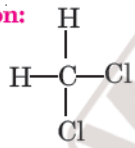
SOLVED EXAMPLES

Example 12.

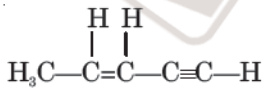
What is the total number of sigma and pi bond in the following molecules :

(i) CH_2Cl_2 *(ii)* $H_3C-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-C\equiv C-H$ *(iii)* C_2H_3Cl

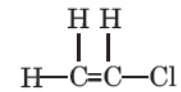
Solution:

(i) 

No. of σ bonds = 4
No. of π bonds = 0

(ii) 

No. of σ bonds = 10
No. of π bonds = 3

(iii) 

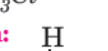
No. of σ bonds = 5
No. of π bonds = 1

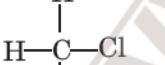
Example 13.

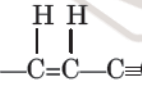
Which hybrid orbitals are used by carbon atoms in the following molecules ?

(i) H_3C-CH_3 *(ii)* $H_3C-CH=CH_2$
(iii) CH_3CHO *(iv)* CH_3COOH
(v) CH_3-CH_2-OH **N.C.E.R.T.**

Solution:

(i)  C–1 and C–2 : sp^3 hybridised,

(ii) 
C–1 : sp^2 hybridised,
C–2 : sp^2 hybridised,
C–3 : sp^3 hybridised

(iii) 
C–1 : sp^3 hybridised,
C–2 : sp^2 hybridised

(iv)
C–1 : sp^3 hybridised,
C–2 : sp^2 hybridised,

(v)
C–1 : sp^3 hybridised
C–2 : sp^3 hybridised

Example 14.

Is there any changes in the hybridisation of B and N atoms as a result of the following reaction :

$BF_3 + NH_3 \longrightarrow F_3B-NH_3$? **N.C.E.R.T.**

Solution: In BF_3, the hybridisation of B is sp^2 and in NH_3, the hybridisation of N is sp^3.

After the reaction, the hybridisation of B changes to sp^3 but the hybridisation of N remains unchanged (sp^3).

The hybridisation and molecular shapes of some molecules are summarised in Table 10.

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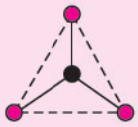
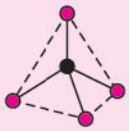
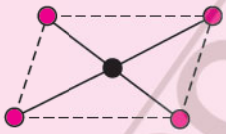
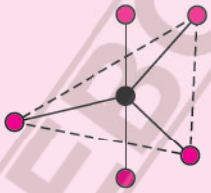
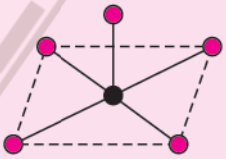
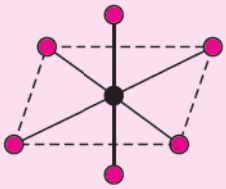
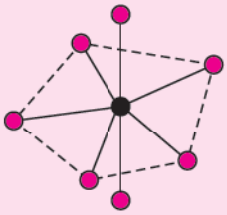
Table 10. Hybrid orbitals and molecular shapes of molecules involving *d*-orbitals

Type of hybridisation	Atomic orbitals	Shape	Bond angle	Examples
sp	$s + p$	Linear	180°	BeH_2, $HgCl_2$ $BeCl_2$, $ZnCl_2$, C_2H_2
sp^2	$s + 2(p)$	 Trigonal planar	120°	BF_3, BCl_3, $AlCl_3$, C_2H_4, CO_3^{2-}, NO_3^-
sp^3	$s + 3(p)$	 Tetrahedral	109.5°	CH_4, $SnCl_4$, $SiCl_4$, SiF_4, NH_4^+, ClO_4^-
dsp^2 (d is $d_{x^2-y^2}$)	$d + s + 2(p)$	 Square planar	90°	$[Ni(CN)_4]^{2-}$, $[Pt\ Cl_4]^{2-}$
sp^3d (d is d_{z^2})	$s + 3\ (p) + d$	 Trigonal bipyramidal	90°, 120°	PF_5, PCl_5
dsp^3 (d is d_{z^2})	$d + s + 3(p)$	 Square pyramidal	90°	BrF_5, $XeOF_4$
sp^3d^2 or d^2sp^3 (d are $d_{x^2-y^2}$, d_{z^2})	$s + 3\ (p) + 2\ (d)$ or $2(d) + s + 3(p)$	 Octahedral	90°	SF_6, CrF_6^{3-} $[Co(NH_3)_6]^{3+}$
sp^3d^3 (d are d_{xy}, d_{yz}, d_{zx})	$s + 3(p) + 3(d)$	 Pentagonal bipyramidal	90° 72°	IF_7

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add on

Conceptual Questions 2

CONCEPTUAL QA

Q. 1. Out of σ and π bonds, which one is stronger bond and why ?

Ans. σ bond is stronger than a π bond. This is because σ-bond is formed by head on overlapping of orbitals and therefore, overlapping is large. On the other hand, π-bond is formed by the sidewise overlapping, which is small.

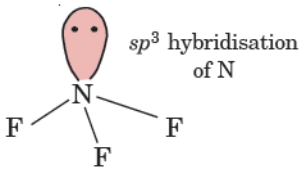
Q. 2. Which of the following molecules will have zero dipole moment :

$SiCl_4$, H_2O, CO_2, BF_3, NH_3 ?

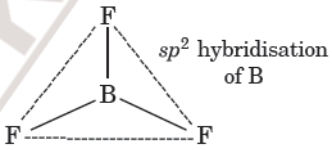
Ans. $SiCl_4$, CO_2 and BF_3 will have zero dipole moment.

Q. 3. Why NF_3 is pyramidal while BF_3 is triangular planar, though both are tetra atomic molecules?

Ans. In NF_3, nitrogen involves sp^3 hybridisation and one position is occupied by a lone pair. Therefore, the molecule is pyramidal. But in BF_3, B involves sp^2 hybridisation having triangular planar geometry.



Pyramidal



Triangular planar

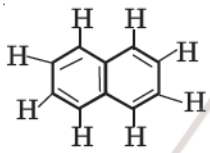
Q. 4. Which of the following has larger bond angle in each pair ?

(*i*) CO_2, BF_3 (*ii*) NH_3, CH_4 (*iii*) H_2O, H_2S (*iv*) SiF_4, C_2H_2

Ans. (*i*) CO_2 (*ii*) CH_4 (*iii*) H_2O (*iv*) C_2H_2

Q. 5. How many σ and π bonds are present in naphthalene ?

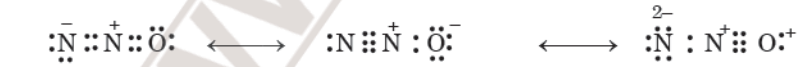
Ans. Naphthalene is



σ bonds = 19, π bonds = 5

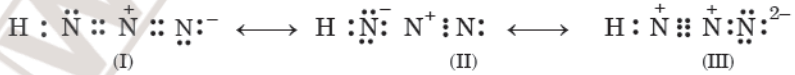
Q. 6. Draw resonating structures of (*i*) nitrous oxide (N_2O) and (*ii*) hydrazoic acid (HN_3) molecule.

Ans. (*i*) Nitrous oxide, N_2O



In this, structure III is unfavourable because it has positive charge on the electronegative oxygen atom and also has electric charges of same sign on the adjacent atoms.

(*ii*) Hydrazoic acid, HN_3



Structure III is unfavourable because of positive charges on adjacent N-atoms and double negative charge on the third N-atom.

Q. 7. Arrange H_2O, NH_3 and CH_4 in the decreasing order of bond angle.

Ans. Bond angle decreases as :

$CH_4 > NH_3 > H_2O$

Q. 8. Benzene ring has alternate single and double bonds, yet all the C–C bonds are of equal lengths. Why ?

Ans. Due to resonance in benzene, all carbon-carbon bonds have same bond lengths (between single and double).

Q. 9. Arrange the following bonds in order of increasing polarity :

P—H, H—O, C—Cl

Ans. Order of polarity is : P—H < C—Cl < H—O

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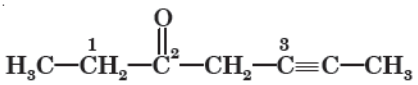
Q. 10. Arrange the following carbon atoms numbered C–1, C–2 and C–3 in the decreasing order of *s*-character :



Ans. Decreasing order of *s*-character

C – 3 > C – 2 > C – 1

Q. 11. Select the molecule or ion having larger property mentioned in each of the following pairs :

(*a*) NF_3, NH_3 : dipole moment

(*b*) NH_3, PH_3 : bond angle

(*c*) CO_2, BF_3 : bond angle

Ans. (*a*) NH_3 (*b*) NH_3 (*c*) CO_2

Q. 12. What type of hybridisation is involved in carbon atoms of benzene ?

Ans. sp^2

Q. 13. Indicate whether the following statement is TRUE or FALSE. Justify your answer in not more than three lines.

The dipole moment of CH_3F is greater than that of CH_3Cl.

Ans. **True**. This is because C–F bond is more polar than C–Cl bond due to larger electronegativity of F than Cl. As a result, the resultant dipole moment of CH_3F is more.

CONCEPTUAL QA

Q. 14. Which of the following has maximum bond angle ?

H_2O, CO_2, NH_3, CH_4

Ans. CO_2 due to its linear structure.

Q. 15. CO_2 is non-polar while H_2O is polar. What conclusion do you draw about their structures from these ?

Ans. CO_2 is a linear molecule, therefore the resultant dipole moment of two C = O bonds get cancelled giving zero dipole moment. On the other hand, water molecule is not linear. It has angular shape and the bond moments of two O–H bonds give resultant dipole moment.

Q. 16. Select the correct choice (no reasons)

(a) Which of the two is more hard : MgO or CaO ?

(b) Which of the two has more ionic character : HCl or HBr ?

Ans. (*a*) MgO, (*b*) HCl

Q. 17. Arrange the following bonds in the order of increasing ionic character : ***N.C.E.R.T.***

C – H, F – H, Br – H, Na – I, K – F and Li – Cl

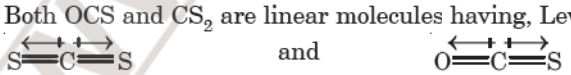
Ans. C – H < Br – H < F – H < Li – Cl < Na – I < K – F.

Q. 18. Arrange the following molecules in order of increasing ionic character of their bonds :
LiF, K_2O, N_2, SO_2, ClF_3 ***N.C.E.R.T.***

Ans. $N_2 < SO_2 < ClF_3 < K_2O <$ LiF

Q. 19. Which of the two molecules OCS and CS_2 has a higher dipole moment and why ? ***N.C.E.R.T.***

Ans Both OCS and CS_2 are linear molecules having, Lewis structure as :

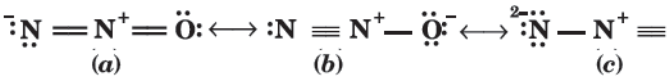


In CS_2, the dipole moment is 0 because the bond moments cancel out. But in OCS, bond moment of C = O is not equal to that of C = S. Hence, it has a net dipole moment. Thus, dipole moment of OCS is higher.

Q. 20. Which type of hybridisation explain the trigonal bipyramidal shape of SF_4 ?

Ans. sp^3d hybridisation.

Q. 21. Nitrous oxide (N_2O) may be represented by the following structures



Which of these contributes least ?

Ans. Structure (*c*) contributes the least because it has positive charge on oxygen atom and has electric charges of same sign on the adjacent atoms.

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MOLECULAR ORBITAL THEORY

Molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The basic idea of molecular orbital theory is that atomic orbitals of individual atoms combine to form molecular orbitals. The electrons in molecules are present in the molecular orbitals which are associated with several nuclei. These molecular orbitals are filled in the same way as the atomic orbitals in atoms are filled.

Salient Features of Molecular Orbital Theory

The salient features of the molecular orbital theory are :

1. Just like an atom, molecule has orbitals of definite energy levels. Like electrons of atoms are present in atomic orbitals, electrons of a molecule are present in different molecular orbitals.

2. Molecular orbitals are formed by the combination of atomic orbitals of proper symmetry and comparable energies. The atomic orbitals of these atoms merge into molecular orbitals.

3. An electron in an atomic orbital is under the influence of only one nucleus. However, an electron in a molecular orbital is under the influence of two or more nuclei depending upon the number of atoms present in the molecule.

Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.

4. Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.

5. ***The number of molecular orbitals formed is equal to the number of combining atomic orbitals***. When two atomic orbitals combine, they form two molecular orbitals. These are called ***bonding molecular orbital*** and ***antibonding molecular orbital***.

6. The bonding MO has lower energy and hence greater stability whereas corresponding antibonding MO has more energy and hence lesser stability.

7. The molecular orbitals are filled in same way as atomic orbitals are filled in accordance with Aufbau principle, Pauli exclusion principle and Hund's rule.

Molecular orbitals are formed by the combination of atomic orbitals of bonded atoms. We have learnt that according to wave mechanics, the atomic orbitals can be expressed by wave functions (ψ's). The wave functions represent the amplitude of the electron waves. These are obtained from the solutions of Schrodinger wave equation. Similarly, we can write Schrodinger wave equation for the whole molecule. However, it is very difficult to solve the wave equation for molecules. To overcome this problem, scientists have used an approximate method known as **linear combination of atomic orbitals abbreviated as LCAO method.**

Formation of Molecular orbitals

According to LCAO method, the orbitals are formed by the linear combination (addition or subtraction) of atomic orbitals of the atoms which form the molecule. Let us apply this theory to hydrogen molecule. Consider that hydrogen molecule consists of two atoms A and B. Each of these atoms has 1*s*-orbital of lowest energy. The atomic orbitals of these atoms may be represented by the wave functions ψ_A and ψ_B for hydrogen atoms A and B respectively. Now, when these atomic orbitals are brought closer, they combine to form molecular orbitals. According to LCAO method, the linear combination of atomic orbitals can take place by addition and by subtraction of wave functions of atomic orbitals.

i.e., $$\psi_{MO} = \psi_A \pm \psi_B$$

These two types of combinations give rise to two molecular orbitals as described below :

(*i*) Molecular orbital obtained by **addition of wave functions** of atoms may be represented as :

$$\psi(MO) = \psi_A + \psi_B$$

$$\text{or} \quad \sigma = \psi_A + \psi_B$$

This molecular orbital is called **bonding molecular orbital.**

(*ii*) Molecular orbital obtained by **subtraction of wave functions** of atoms may be represented as :

$$\psi^*(MO) = \psi_A - \psi_B$$

$$\text{or} \quad \sigma^* = \psi_A - \psi_B$$

The molecular orbital is called **antibonding molecular orbital.**

The physical picture of bonding and antibonding molecular orbitals can be obtained by considering the atomic orbitals. To illustrate this, we may take the combination of 1*s*-orbital of one hydrogen atom with 1*s*-orbital of second hydrogen atom to form two molecular orbitals in hydrogen molecule. As discussed above, there are two ways of combining atomic orbitals. The molecular orbital formed by the addition of overlapping of two 1*s*-orbitals is shown in Fig. 47. It is clear from the figure that the region between the two nuclei where the two 1*s*-atomic orbitals overlap has high electron density. Therefore, repulsion between the nuclei is very less. Such a molecular orbital is called **bonding molecular orbital.** It is designated as σ 1*s* (called sigma 1*s*) orbital. The sigma (σ) signifies that the orbital is symmetrical about the molecular axis and the script '1*s*' indicates that it is formed by the combination of 1*s*-atomic orbitals.

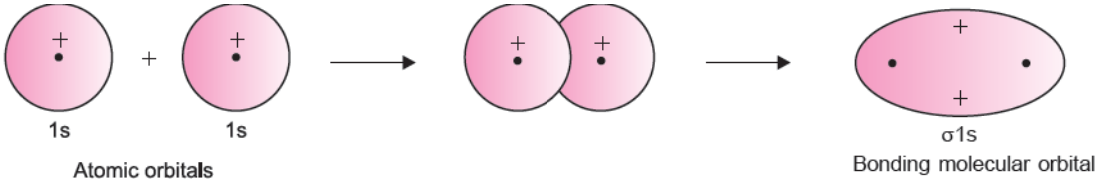

Fig. 47. Formation of bonding molecular orbital.

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The molecular orbital formed by the subtraction of overlapping of two 1*s*-orbitals is shown in Fig. 48.

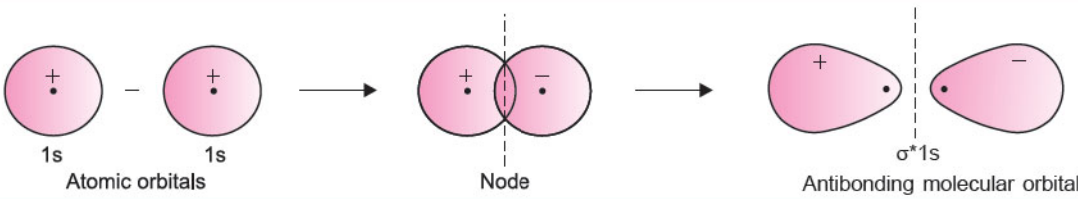

Fig. 48. Formation of antibonding molecular orbital.

It is clear from the figure that the electron density in between the two nuclei is practically zero and most of the electron density is located away from the space between the two nuclei. This is because, the electron probability densities of two atomic orbitals get cancelled in the centre (by subtraction) so that there is no probability of finding the electron in the region of overlap *i.e.* between the nuclei. In fact, there is a nodal plane (on which the electron density is zero) between the nuclei and hence the repulsion between the nuclei is high. This situation does not favour the bond formation. Such an orbital is called **anti-bonding molecular orbital.** It is designated as σ*1*s* (called sigma star 1*s*). The asterisk '*' is used to represent antibonding molecular orbital.

Thus, **the bonding molecular orbital is designated as σ 1*s* (called sigma bonding) and antibonding molecular orbital is designated as σ* 1*s* (called sigma antibonding).**

Differences between atomic and molecular orbitals

The important differences between atomic and molecular orbitals are :

Atomic orbital	Molecular orbital
1. An electron in atomic orbital is under the influence of only one positive nucleus of the atom.	An electron in molecular orbital is under the influence of two or more nuclei depending upon the number of atoms present in the molecule.
2. Atomic orbitals are inherent property of an atom.	Molecular orbitals are formed by the combination of atomic orbitals.
3. They have simple shapes.	They have complex shapes.

The formation of bonding and antibonding molecular orbitals can be explained in terms of *constructive interference (or additive effect) and destructive interference (or subtractive effect)* of the electron waves of the combining atoms.

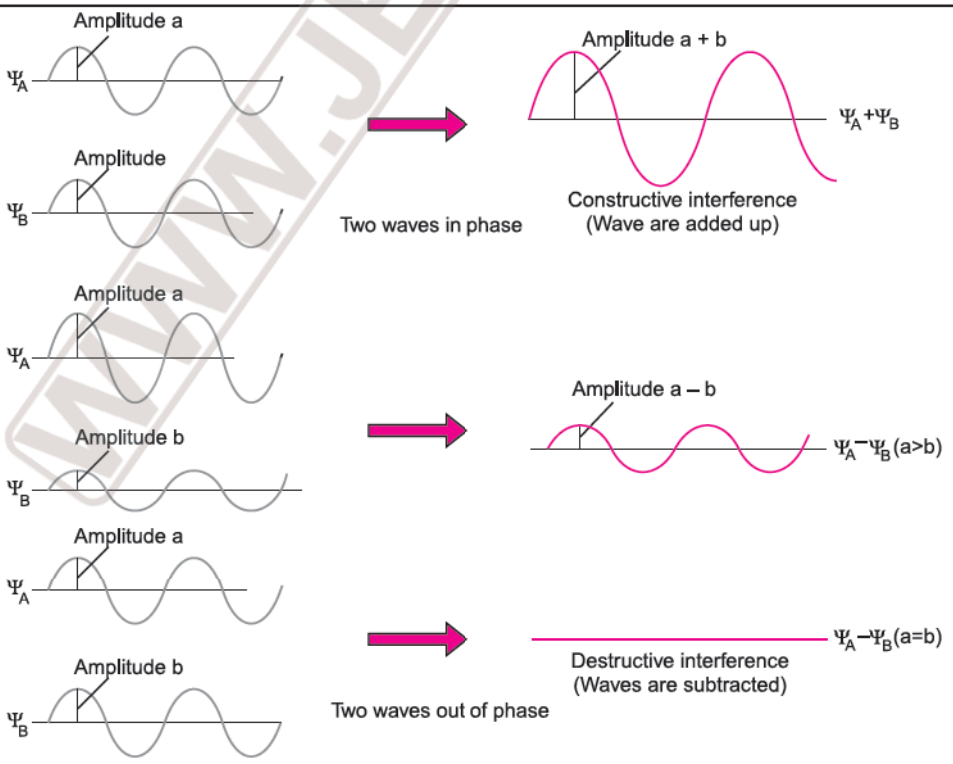

Fig. 49. Constructive and destructive interference of waves.

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(*i*) **During constructive interference**, *the two waves are in phase* and the amplitudes of the waves get *added up*. Therefore, the resulting wave function has more electron density in between the nuclei. This corresponds to bonding MO.

(*ii*) On the other hand, when the *two waves are out of phase,* there is **destructive interference** and the amplitudes of the waves get *subtracted* or *cancelled.* Therefore, the resulting wave function has less electron density between the nuclei. This also gives rise *to nodal plane between two nuclei.* This corresponds to wave function of antibonding MO.

The probability density in bonding and antibonding MOs can also be shown by simple mathematics. We know that the probability density is given by square of wave function (ψ^2).

For bonding MO,

$$\psi = \psi_A + \psi_B, \quad \text{so that}$$

$$\psi^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + \mathbf{2\psi_A \psi_B}$$

Thus, ψ^2 is greater than $\psi_A^2 + \psi_B^2$ (sum of the probability densities of individual atoms) by an amount equal to $2\psi_A \psi_B$. Therefore, *the probability of finding electrons in the bonding MO is greater than in either of atomic orbitals* (ψ_A or ψ_B).

For antibonding MO,

$$\psi^* = \psi_A - \psi_B, \text{ so that}$$

$$\psi^{*2} = (\psi_A - \psi_B)^2 = \psi_A^2 + \psi_B^2 - \mathbf{2\psi_A \psi_B}$$

Thus, ψ^{*2} is less than $\psi_A^2 + \psi_B^2$ by an amount equal to $2\psi_A \psi_B$. Therefore, *the probability of finding the electrons in antibonding MO is less than that in either of the atomic orbitals* (ψ_A or ψ_B).

Note. The positive signs in the *s*-orbitals in Figs. 47 and 48 correspond to the signs of the wave function ψ's. The wave function may have + or – signs.
These signs correspond to + and – signs of the waves. It may be noted that crests of the electron wave are usually given '+' sign and the troughs are given '–' sign. The bonding MO is obtained by the combination of '+' with '+' or '–' with '–' part of the electron wave. On the other hand, antibonding MO is obtained by the combination of '+' with '–' part. To understand the overlapping of two bonding orbitals, it is necessary to give + or – signs of wave functions. It may be remembered that *s*-orbitals are spherically symmetrical and are +ve in all directions while the *p*-orbitals consisting of two lobes have one lobe with + ve sign and the other lobe with – ve sign (unit 2).

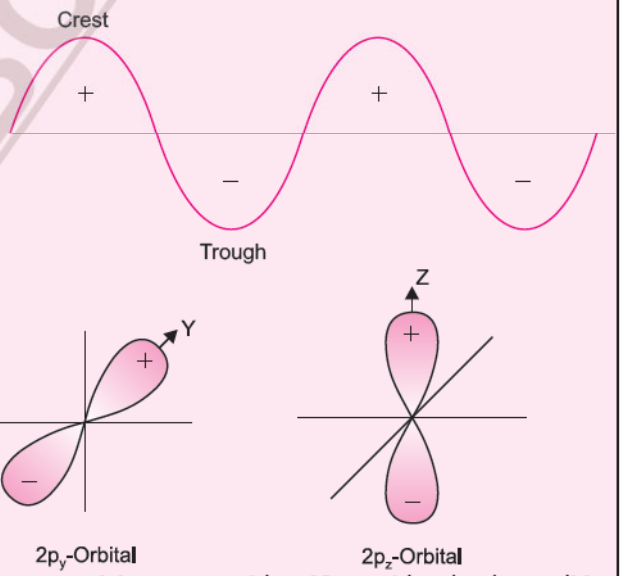

Fig. 50. During overlapping or combination of atomic orbitals, only + + or – – lobes can combine. No combination is possible between + and – lobes.

It must be remembered that these '+' and '–' signs have nothing to do with the electrical charges on the orbitals.

RELATIVE ENERGIES OF BONDING AND ANTIBONDING MOLECULAR ORBITALS

We have learnt that in the case of bonding molecular orbital, the attraction of both the nuclei for both the electrons is increased. This results in lowering of energy. In the case of antibonding molecular orbital, the electrons try to go away from the nuclei and this corresponds to repulsive state. The energy of this orbital will be higher. The relative energies of bonding and antibonding molecular orbitals along with atomic orbitals can be represented as shown in Fig. 51.

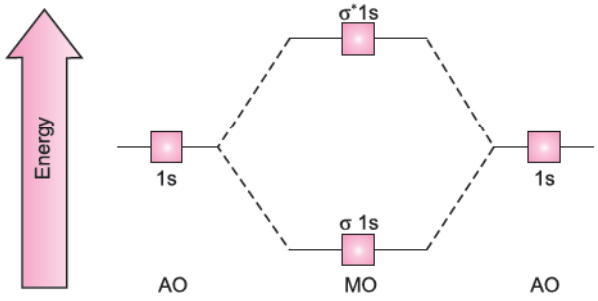

Fig. 51. Relative energies of σ 1*s* and σ*1*s* molecular orbitals.

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Thus, the *bonding* molecular orbital is *stabilized* relative to the energy of the isolated atoms and *anti-bonding* molecular orbital is *destabilized* relative to the individual atoms. Further, it may be noted that *the bonding MO is stabilized to the same extent as the antibonding MO is destabilized.*

Differences between Bonding and Anti-bonding Molecular Orbitals

Bonding MO	Anti-bonding MO
1. Bonding molecular orbital is formed by the addition of overlapping of atomic orbitals. The wave function of the bonding MO may be written as : $\psi(MO) = \psi_A + \psi_B$	Anti-bonding molecular orbital is formed by the subtraction of overlapping of atomic orbitals. The wave function for the ant-bonding MO may be written as : $\psi^*(MO) = \psi_A - \psi_B$
2. They are formed when the lobes of the combining atomic orbitals have same sign.	They are formed when the lobes of the combining atomic orbitals have opposite sign.
3. It has greater electron density in the region between the two nuclei of bonded atoms.	It has lesser electron density in the region between the two nuclei of the atoms.
4. The forces in this orbital tend to bring the two nuclei of the atoms together. Therefore, the electrons in the bonding MO contribute to attraction between the two atoms.	The forces in this orbital push the nuclei apart. Therefore, the electrons in antibonding MO contribute to repulsion between the atoms.
5. It possesses lower energy than the isolated atomic orbitals.	It possesses higher energy than the isolated atomic orbitals.

COMBINATION OF 2*s* AND 2*p* ATOMIC ORBITALS TO FORM MOLECULAR ORBITALS

Combination of 2*s* atomic orbitals

Like 1*s*-orbitals, 2*s*-orbitals combine by addition and subtraction of overlapping to form bonding and antibonding molecular orbitals. These are labelled as $\sigma 2s$ and $\sigma^* 2s$. These molecular orbitals have exactly the same shapes as $\sigma 1s$ and $\sigma^* 1s$ MOs but they are slightly larger in size.

Combination of 2*p* atomic orbitals

There are three *p*-orbitals namely $2p_x$, $2p_y$ and $2p_z$ which are directed in space along the *x*, *y* and *z* coordinate axes respectively. By convention, ***we can assume z-axis as the internuclear axis.*** The *x* and *y*-axes would then be perpendicular to the internuclear axis. The combination of 2*p*-orbitals forms two types of MOs; sigma (σ) MOs and pi (π) MOs as discussed below :

(*i*) Formation of σ-molecular orbitals. When the two $2p_z$ orbitals are brought closer along the internuclear axis, they overlap head on forming σ-bond (Fig. 52). When the two orbitals overlap by the addition of electron waves (*i.e.*, with proper signs, ++ lobes overlap), bonding molecular orbital is formed. This may be designated as $\sigma 2p_z$. On the other hand, when the two wave functions are subtracted, an antibonding molecular orbital is formed. This is designated as $\sigma^* 2p_z$. Thus, two $2p_z$ atomic orbitals combine to form two molecular orbitals, *i.e.* a bonding M.O. ($\sigma 2p_z$) and an antibonding M.O. ($\sigma^* 2p_z$).

(*ii*) Formation of π-molecular orbitals. When a $2p_x$ atomic orbital of one atom approaches the $2p_x$ atomic orbital of another atom, the overlapping occurs sidewise and not end-to-end. *The molecular orbital formed by sidewise or lateral overlap is known as pi (π) molecular orbital.* The molecular orbital formed is not symmetrical about the internuclear axis. The molecular orbital formed by overlapping of two $2p_x$ atomic orbitals by the addition of electron waves is called *bonding pi molecular orbital* designated as $\pi\, 2p_x$ while the molecular orbital formed by the overlapping of two $2p_x$ atomic orbitals by the subtraction of electron waves is called *antibonding molecular orbital* labelled as $\pi^* 2p_x$. These are shown in Fig. 53.

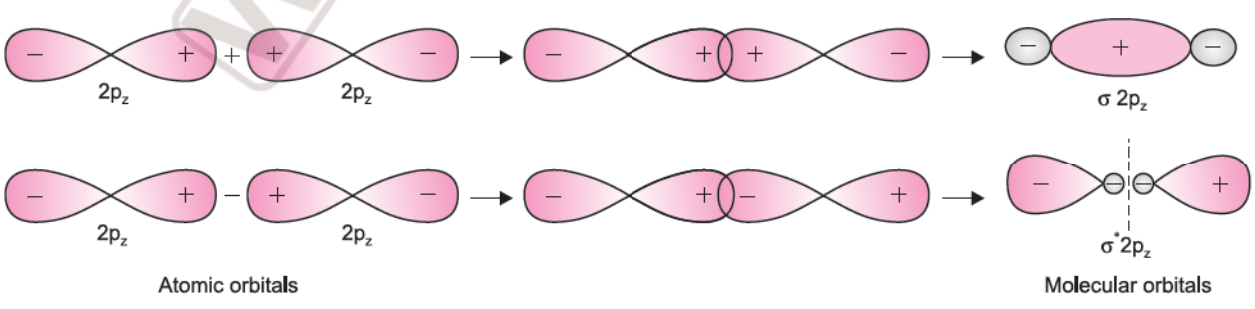

Fig. 52. Bonding ($\sigma 2p_z$) and antibonding ($\sigma^* 2p_z$) molecular orbitals from $2p_z$ atomic orbitals.

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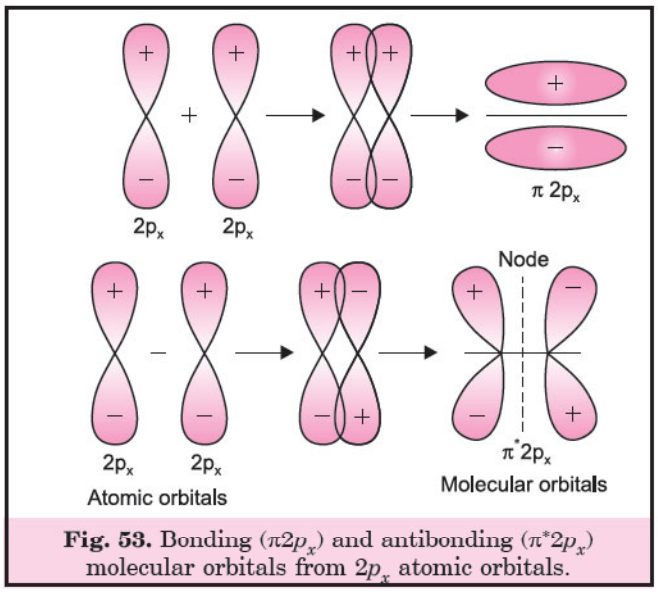

Fig. 53. Bonding ($\pi 2p_x$) and antibonding ($\pi^* 2p_x$) molecular orbitals from $2p_x$ atomic orbitals.

Similarly, when a $2p_y$ orbital of one atom overlaps with a $2p_y$ orbital of another atom, they also overlap sidewise forming two molecular orbitals $\pi 2p_y$ and $\pi^* 2p_y$. These are exactly similar to $\pi 2p_x$ and $\pi^* 2p_x$ MOs.

Differences between σ and π Molecular Orbitals

σ MO	π MO
1. It is formed by the head-to-head overlap of AOs *i.e*, along internuclear axis.	It is formed by sidewise overlap of AOs perpendicular to internuclear axis.
2. The overlap region is maximum.	The overlap region is minimum.
3. The orbital is symmetrical to rotation about internuclear axis.	The orbital is not symmetrical to rotation about internuclear axis.
4. It leads to the formation of a strong bond.	It leads to the formation of a weak bond.

CONDITIONS FOR THE COMBINATION OF ATOMIC ORBITALS

Molecular orbitals are formed by the combination of atomic orbitals. But all types of orbitals cannot combine with each other. The following are the **main conditions for effective combination of atomic orbitals:**

1. ***The combining atomic orbitals must have same or nearly the same energies.*** For example, in case of homonuclear diatomic molecules of the type A_2, 2*s*-orbital of one atom can combine with 2*s*-orbital of another atom but 1*s*-orbital of one atom cannot combine with 2*s*-orbital of another atom.

2. ***The extent of overlapping between the atomic orbitals of two atoms should be large.*** Greater the extent of overlap, the greater will be the electron density between the nuclei of a molecular orbital.

3. ***The combining atomic orbitals must have the same symmetry (or proper orientation) about the moecular axis.***

For example, if we take *z*-axis as the internuclear axis, $2p_z$ orbital of one atom can combine with $2p_z$ orbital of other atom but $2p_z$ orbital of one atom cannot combine with $2p_x$ or $2p_y$ orbitals of other atom because of their different orientations or symmetries.

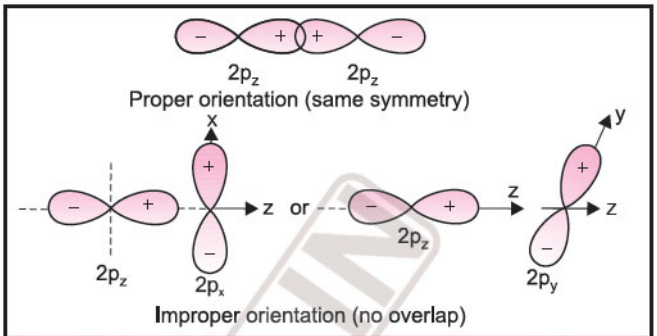

Fig. 54. Possibility of combination of $2p_z$ and $2p_z$ and impossibility of combination of $2p_z$ and $2p_x$ or $2p_z$ and $2p_y$.

Similarly a 2*s*-orbital of one atom can combine with $2p_z$ orbital of another atom [Fig. 55(a)] but it cannot overlap with $2p_x$ or $2p_y$ orbital of another atom. When 2*s*-orbital of one atom A overlaps with $2p_x$ orbital of another atom B [Fig. 55(b)], ++ overlap is cancelled by the + – overlap. As a result, no molecular orbital is formed. In other words, such a combination (2*s* with $2p_x$ or 2*s* with $2p_y$) is not possible.

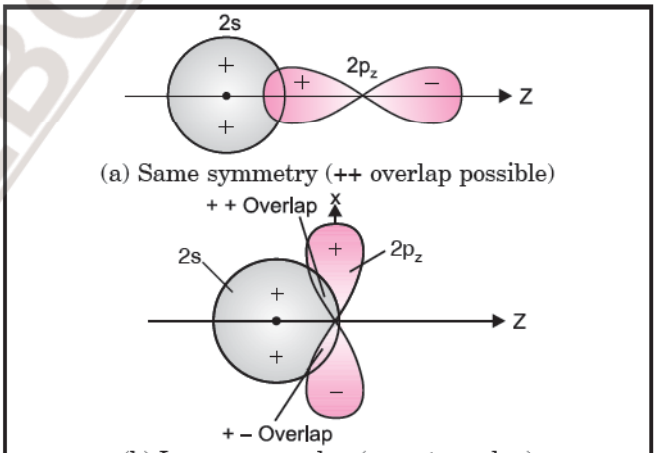

Fig. 55. Possibility of combination of 2*s* and $2p_z$ atomic orbitals and absence of combination of 2*s* and $2p_x$ atomic orbitals.

SOLVED EXAMPLES

Example 15.

Label the molecular orbitals formed by the following combinations of atomic orbitals (Assume z-axis as internuclear axis) :

(i) $2s + 2s$ *(ii)* $2p_x - 2p_x$ *(iii)* $2p_z + 2p_z$ *(iv)* $1s - 1s$ *(v)* $2p_y + 2p_y$.

Solution : The MOs formed are :

(i) $2s + 2s = \sigma 2s$ *(ii)* $2p_x - 2p_x = \pi^* 2p_x$
(iii) $2p_z + 2p_z = \sigma 2p_z$ *(iv)* $1s - 1s = \sigma^* 1s$
(v) $2p_y + 2p_y = \pi 2p_y$

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Practice Problems

18. If z-axis is the internuclear axis, which of the following combinations are not allowed ?
(i) $2s$ and $2s$ *(ii)* $1s$ and $2p_x$ *(iii)* $2p_y$ and $2p_y$
(iv) $2p_x$ and $2p_z$ *(v)* $2p_z$ and $2p_z$ *(vi)* $2s$ and $2p_z$
(vii) $2p_x$ and $2p_y$.

19. Which of the following combinations of atomic orbitals will give antibonding π-molecular orbital (assume z-axis as internuclear axis):
(i) $2s + 2p_z$ *(ii)* $2p_y + 2p_y$ *(iii)* $2p_x - 2p_x$ *(iv)* $2p_z - 2p_z$.

Answers to Practice Problems

18. *(ii), (iv), (vii)* **19.** *(iii)*

ENERGY LEVEL DIAGRAM FOR MOLECULAR ORBITALS

The relative energies of molecular orbitals depend upon the following two factors :

(i) the energies of the AOs combining to form MOs.

(ii) the extent of overlapping between the atomic orbitals. The greater the overlap, the more the bonding orbital is lowered and the anti-bonding orbital is raised in energy relative to AOs. For example, the extent of overlapping in case of σ-orbital is more than that in π-orbital. Consequently, the energy of σ $2p_z$ is lower than the energy of bonding π $2p_x$ or π $2p_y$ MOs.

Now, $1s$ AOs of two atoms form two MOs designated as σ$1s$ and σ*$1s$. The $2s$ and $2p$ orbitals (eight AOs on two atoms) form four bonding MOs and four anti-bonding MOs as :

Bonding MOs : $\sigma 2s,\ \sigma 2p_z,\ \pi 2p_x,\ \pi 2p_y$

Anti-bonding MOs : $\sigma^*2s,\ \sigma^*2p_z,\ \pi^*2p_x,\ \pi^*\ 2p_y$

The energy levels of these molecular orbitals have been determined experimentally by spectroscopic methods. The order of increasing energy of molecular orbitals obtained by the combination of $1s$, $2s$ and $2p$ orbitals of two atoms is :

$$\sigma 1s, \sigma^*1s, \sigma 2s, \sigma^*2s, \sigma 2p_z, \pi 2p_x = \pi 2p_y, \pi^*2p_x = \pi^*2p_y, \sigma^*2p_z$$

Energy increases

However, experimental evidence for some diatomic molecules have shown that above sequence of energy levels of MOs is not correct for all molecules. For example, for homonuclear diatomic molecules of second row elements such as Li_2, Be_2, B_2, C_2, N_2, **the σ$2p_z$ MO is higher in energy than π$2p_x$ and π$2p_y$ MOs.** The order of MOs for these molecules is

$$\sigma 1s, \sigma^*1s, \sigma 2s, \sigma^*2s, \pi 2p_x = \pi 2p_y, \sigma 2p_z, \pi^*2p_x = \pi^*2p_y, \sigma^*2p_z$$

Energy increases

But for molecules O_2 onwards (O_2, F_2), the first order of energies of MOs is correct.

Thus, for diatomic molecules of second period (Li_2 to Ne_2), there are two types of energy levels of MOs as shown in Fig. 56. For molecules Li_2, Be_2, B_2, C_2 and N_2 the molecular orbital energy level diagram is shown in Fig. 56 (*a*). On the other hand, for the molecules O_2, F_2 and Ne_2 the molecular orbital energy level diagram is shown in Fig. 56 (*b*).

The main difference between the two types of sequences is that for molecules O_2, F_2 and Ne_2, the σ$2p_z$ MO is lower in energy than π$2p_x$ and π$2p_y$ MOs while in the case of molecules Li_2, Be_2, B_2, C_2 and N_2, σ$2p_z$ MO has higher energy than π$2p_x$ and π$2p_y$ MOs.

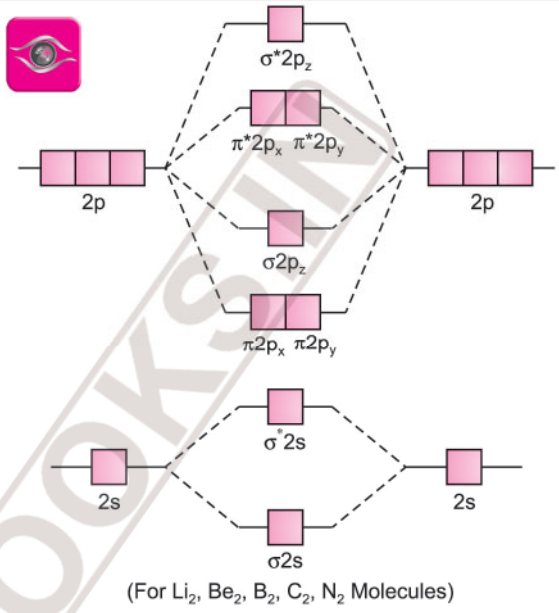

Fig. 56. (*a*) Molecular orbital energy level diagram for Li_2, Be_2, B_2, C_2 and N_2 molecules.

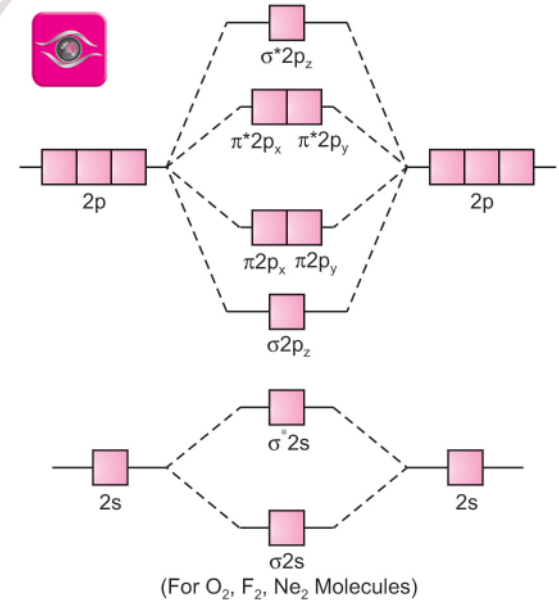

Fig. 56. (*b*) Molecular orbital energy level diagram for O_2, F_2 and Ne_2 molecules.

The main reason for the difference in sequences is the interaction of 2s and $2p_z$ AOs. For the molecules Li_2, Be_2, B_2, C_2 and N_2, the differences in energies of 2s and $2p_z$ orbitals is small and, therefore, they can interact. While the energies of 2s and $2p_z$ AOs for O_2, F_2 and Ne_2 is large and therefore, they cannot interact. The discussion is beyond the scope of the present book.

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RULES FOR FILLING MOLECULAR ORBITALS

The following rules are followed for filling up molecular orbitals with electrons in order to write molecular configurations :

1. The molecular orbital having the lowest energy is filled first. This is in accordance with ***Aufbau principle*** as already discussed for atoms.
2. Each molecular orbital can accommodate maximum of two electrons having opposite spins. This is in accordance with ***Pauli's exclusion principle.***
3. If there are two molecular orbitals of the same energy, the pairing of electrons will occur only after each orbital of same energy has one electron. This is in accordance with ***Hund's rule.***

ELECTRONIC CONFIGURATIONS AND MOLECULAR BEHAVIOUR

The distribution of electrons among various molecular orbitals is called the **electronic configuration of the molecule.** The electronic configuration of the molecule or the molecular orbital energy level diagram gives the following information, regarding the behaviour of molecules.

(*a*) Stability of a molecule. The electrons in bonding molecular orbitals will give stability to the molecule whereas those in antibonding molecular orbitals will decrease the stability. Thus, if N_b represents the number of electrons in bonding molecular orbitals and N_a represents the number of electrons in anti-bonding molecular orbitals, then the following generalization can be made :

(i) The molecule is stable if $N_b > N_a$.

(ii) The molecule is unstable if $N_b < N_a$.

(iii) The molecule is unstable if $N_b = N_a$.

- According to *(i)*, more bonding molecular orbitals are occupied and therefore, the bonding influence is stronger and therefore, a stable molecule is formed.
- In *(ii)*, the anti-bonding influence is stronger and hence the molecule is unstable.
- According to *(iii)*, even if the number of electrons in bonding MOs and the number of electrons in anti-bonding MOs are same, the atoms do not combine to form molecules. *This is because of the fact that the effect of anti-bonding electrons is slightly more than that of bonding electrons.*

(b) Bond order. It is defined *as the number of covalent bonds in a molecule.* It is equal to **one half of the difference between the number of electrons in the bonding and antibonding molecular orbitals.**

$$\text{Bond order} = \frac{\left[\begin{matrix}\text{No. of electrons}\\ \text{in bonding MOs}\end{matrix}\right] - \left[\begin{matrix}\text{No. of electrons}\\ \text{in anti-bonding MOs}\end{matrix}\right]}{2}$$

or $$= \frac{N_b - N_a}{2}$$

The bond orders of 1, 2 or 3 correspond to single, double or triple bond. But bond order may be fractional also in some cases.

Information Conveyed by Bond Order

The bond order conveys the following important informations :

(i) If the value of bond order is positive, it indicates a stable molecule and if the value of bond order is negative or zero, it means that the molecule is unstable.

(ii) The stability of a molecule is measured by its bond dissociation energy. But *the bond dissociation energy is directly proportional to the bond order.* **Greater the bond order, greater is the bond dissociation energy.** For example, nitrogen molecule with bond order equal to 3 has larger bond dissociation energy (945 kJ mol^{-1}) than oxygen molecule (bond dissociation energy 495 kJ mol^{-1}) with a bond order equal to 2.

(iii) Bond order is inversely proportional to the bond length. The higher the bond order value, smaller is the bond length. For example, the bond length in nitrogen molecule is shorter than in oxygen molecule as shown below :

Molecule	Bond order	Bond Dissociation energy	Bond length
Oxygen	2	495 kJ mol^{-1}	121 pm
Nitrogen	3	945 kJ mol^{-1}	110 pm

(*c*) Magnetic character. If all the electrons in the molecule of a substance are paired, the substance is **diamagnetic** (repelled by the magnetic field)**.** On the other hand, if there are unpaired electrons in the molecule, the substance is **paramagnetic** (attracted by the magnetic field).

BONDING IN SOME DIATOMIC MOLECULES

Let us discuss bonding in some homonuclear diatomic molecules of the elements of first and second rows of the periodic table.

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1. Hydrogen molecule (H_2). Each hydrogen atom has one electron in 1*s*-orbital and, therefore, there are two electrons in hydrogen molecule. Both these electrons are to be accommodated in the lowest energy molecular orbital. According to Pauli's exclusion principle, these two electrons should have opposite spins. The molecular orbital energy level diagram for H_2 molecule is shown in Fig. 57.

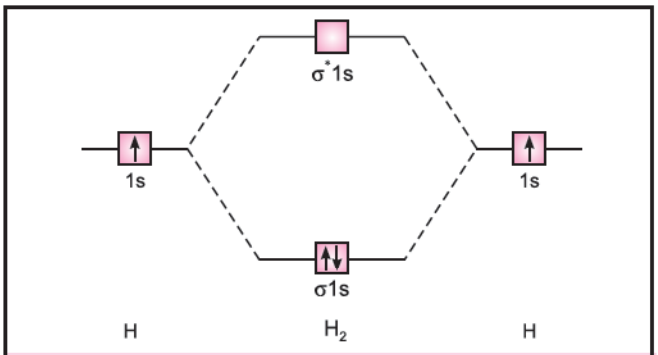

Fig. 57. Molecular orbital energy level diagram for H_2 molecule.

The molecular orbital electronic configuration of H_2 molecule is :

$$H_2 : (\sigma\, 1s)^2$$

The bond order in H_2 is :

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

The bond dissociation energy of hydrogen molecule has been found to be 438 kJ mol^{-1} and bond length equal to 74 pm. Moreover, since no unpaired electron is present in hydrogen molecule, it is **diamagnetic.**

2. Hydrogen molecule ion (H_2^+). This is formed by the combination of hydrogen atom containing one electron and hydrogen ion having no electron. Therefore, this ion has only one electron. The molecular orbital diagram is given in Fig. 58.

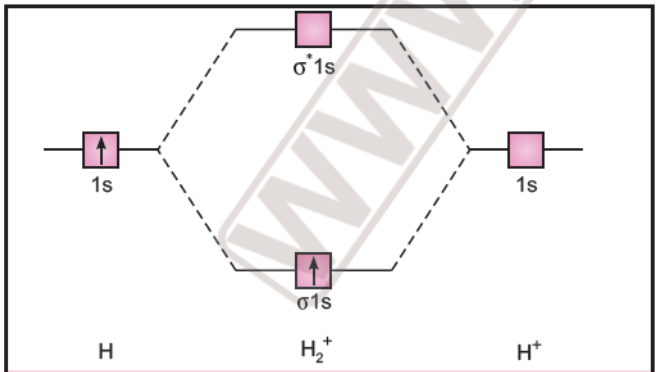

Fig. 58. Molecular orbital energy level diagram for H_2^+ ion.

The electronic configuration of the molecule ion is:

$$H_2^+ : (\sigma\, 1\, s)^1$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{1-0}{2} = \frac{1}{2}$$

The positive value of bond order indicates that the molecule is stable. The presence of unpaired electron in the molecule indicates that it is **paramagnetic** molecule.

The bond length of H_2^+ ion is larger than that of H_2 molecule (bond length H_2^+ = 104 pm; H_2 = 74 pm) while its bond dissociation energy is less than that of H_2 molecule (bond dissociation energy H_2^+ = 269 kJ mol^{-1}, H_2 = 458 kJ mol^{-1}). *This clearly supports the fact that bond in H_2^+ ion is weaker than that in H_2 molecule.*

3. Hypothetical helium molecule (He_2). Each helium atom has two electrons in 1*s*-orbital, and therefore, there are four electrons in He_2 molecule. These electrons will be accommodated in σ1*s* and σ*1*s* MOs as shown in Fig. 59. The electronic configuration for helium molecule may be written as :

$$He_2 : (\sigma\, 1s)^2\, (\sigma^*\, 1s)^2$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-2}{2} = 0.$$

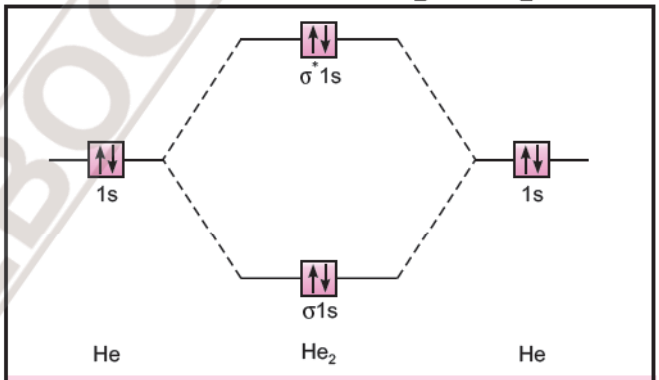

Fig. 59. Molecular orbital energy level diagram for He_2 molecule (hypothetical).

The **zero bond order value indicates that there is no net bonding and He_2 molecule should not be formed.** In fact, there is no experimental evidence for the existence of this molecule.

4. Helium molecule ion (He_2^+). This molecule contains three electrons, two from one helium atom and one from the other (He^+ ion). The molecular orbital electronic configuration of the molecule ion is

$$He_2^+ : (\sigma\, 1s)^2\, (\sigma^*\, 1s)^1$$

$$\text{Bond order} = \frac{2-1}{2} = \frac{1}{2}$$

The value of bond order indicates that He_2^+ is stable. Its bond dissociation energy has been found to be 242 kJ mol^{-1}. The molecule is expected to be **paramagnetic** and the same has been experimentally observed also.

5. Lithium molecule (Li_2). The electronic configuration of lithium is $1s^2 2s^1$. There are six electrons in lithium molecule. The electronic configuration of Li_2 molecule may be written as :

$$Li_2 : (\sigma 1s)^2\, (\sigma 1s^*)^2\, (\sigma 2s)^2$$

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The above configuration may also be written as :

$$KK\ (\sigma 2s)^2$$

where KK represents fully filled inner K shells in two atoms i.e. $(\sigma 1s)^2\,(\sigma 1^*s)^2$

From the electronic configuration of Li_2 molecule, it is clear that there are 4 electrons in bonding MOs and 2 electrons in antibonding MOs.

Therefore, its bond order is :

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{4-2}{2} = 1$$

Thus, there is one Li—Li sigma bond. The bond energy of the molecule is quite low, being about 110 kJ mol^{-1}. The bond length of the molecule is 265 pm. Since it has no unpaired electrons, it should be diamagnetic. Indeed diamagnetic Li_2 molecules are known to exist in the vapour phase.

Comparison of Li—Li and H—H bonds. The comparison of Li—Li and H—H bonds reveals that the sigma bond in Li_2 molecule is weaker and much longer than σ-bond in H_2 molecule. This may be attributed to the following reasons :

(*i*) The 2*s* orbital of lithium is bigger in size than the 1*s* orbital. Therefore, the overlapping of 2*s*—2*s* atomic orbitals is less effective than the overlapping of 1*s*—1*s* orbitals.

(*ii*) In lithium molecule, the outer electrons in $(\sigma 2s)$ molecular orbital are shielded by the inner 1*s* electrons. Therefore, the attraction between the nuclei and the electrons in $(\sigma 2s)$ molecular orbital is less.

Moreover, the inner $1s^2$ electrons of two lithium atoms cause repulsion between the atoms. Therefore, they do not allow them to come closer.

6. Beryllium molecule, (Be_2). Beryllium (Z = 4) has electronic configuration $1s^2 2s^2$. In the formation of a diatomic molecule, evidently, two outer electrons of each atom, *i.e.*, four in all, have to be accommodated in molecular orbitals. Two of these go into the bonding $(\sigma 2s)$ orbital while the other two have to go into the anti-bonding (σ^*2s) orbital.

The molecular orbital electronic configuration is :

$$Be_2 : KK(\sigma 2s)^2\,(\sigma^*2s)^2$$

$$\text{bond order} = \frac{1}{2}(2-2) = 0$$

The **zero bond order** suggests that Be_2 molecule does not exist.

7. Boron molecule, (B_2). The electronic configuration of boron is $1s^2\ 2s^2\ 2p^1$. The outermost shell of each atom contains 3 electrons. When two B atoms combine to form molecule B_2, there are 6 electrons which need to be accommodated in the molecular orbitals of B_2. The molecular orbital electronic configuration is :

$$B_2 : KK(\sigma 2s)^2\,(\sigma^*2s)^2\,(\pi 2p_x)^1\,(\pi 2p_y)^1$$

$$\text{bond order} = \frac{1}{2}(4-2) = 1$$

The molecule has only one bond. The electrons which contribute towards bonding are the $\pi 2p_x$ and $\pi 2p_y$ MOs. This indicates that the molecule is formed by a weak π-bond. The bond dissociation energy of B_2 molecule has been found to be 290 kJ mol^{-1} and bond length equal to 159 pm.

Since each $\pi 2p_x$ and $\pi 2p_y$ MO contains single electron, the molecule B_2 is **paramagnetic.**

8. Carbon molecule, (C_2). The electronic configuration of carbon is $1s^2\ 2s^2\ 2p^2$. The outer shell of each atom contains 4 electrons. In the formation of C_2 molecule, there will be evidently 8 electrons to be accommodated in the outer molecular orbitals of C_2. The molecular orbital electronic configuration is :

$$C_2 : KK\ (\sigma 2s)^2\ \ (\sigma^*2s)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2$$

$$\text{bond order} = \frac{1}{2}(6-2) = 2$$

Thus, the C_2 molecule has two bonds. The bond dissociation energy of C_2 molecule has been found to be 620 kJ mol^{-1} and bond length equal to 131 pm.

Further, since C_2 molecule does not have any unpaired electron, it is ***diamagnetic.*** The diamagnetic C_2 molecule has been detected in vapour phase.

It may be noted that double bond in C_2 molecule consists of both the *pi* bonds because of the presence of 4 electrons in two *pi* MOs. In most of the other molecules, a double bond is made up of a sigma bond and a *pi* bond.

9. Nitrogen molecule (N_2). The electronic configuration of nitrogen atom is $1s^2\ 2s^2\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$ and N_2 molecule has 14 electrons. The M.O. diagram is shown in Fig. 60.

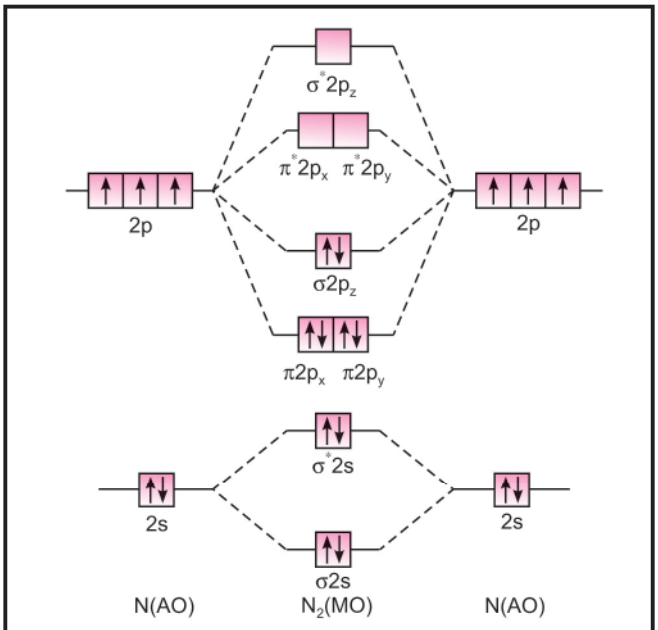

Fig. 60. Molecular orbital energy level diagram for N_2 molecule.

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The molecular orbital electronic configuration of the molecule is :

$$N_2 : KK\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2$$

$$\text{Bond order} = \frac{8-2}{2} = 3.$$

Thus, nitrogen molecule has **three bonds,** one σ and two π-bonds. This is in accordance with very high bond dissociation energy (945 kJ mol^{-1}) and small bond length (110 pm) of the molecule. The molecule is **diamagnetic** because there are no unpaired electrons.

Comparison of N_2 and N_2^+ ion

N_2^+ ion is formed by the removal of one electron from N_2 molecule. This electron will be lost from $2p_z$ M.O. Hence the electronic configuration of N_2^+ ion will be

$$N_2^+ : KK\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^1$$

$$\text{Bond order} = \frac{7-2}{2} = 2\frac{1}{2}$$

Since bond order of N_2^+ ion (2.5) is less than the bond order of N_2 (3) molecule, therefore, the bond strength of N_2^+ will be less than that of N_2 molecule and bond length of N_2^+ will be more than that of N_2 molecule.

10. Oxygen molecule (O_2). The electronic configuration of oxygen atom is $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$. Therefore, oxygen molecule has 16 electrons. In the formation of molecular orbitals, the electrons in the inner shells are expressed as KK denoting $(\sigma 1s)^2$ $(\sigma^* 1s)^2$. The remaining 12 electrons are filled in molecular orbitals as shown in Fig. 61.

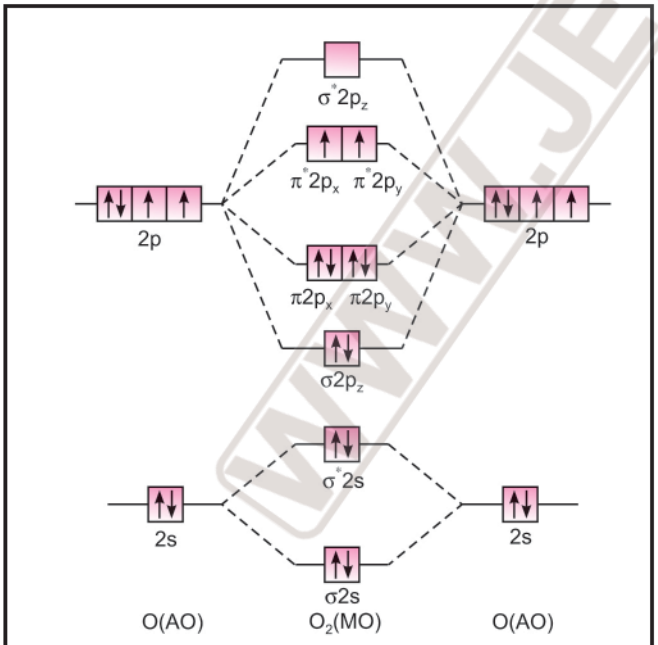

Fig. 61. Molecular orbital energy level diagram for O_2 molecule.

The electronic configuration of the molecule is :

$$O_2 : KK\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^1\ (\pi^* 2p_y)^1$$

$$\text{Bond order} = \frac{8-4}{2} = 2$$

Thus, oxygen molecule has **two bonds** (one σ and one π). Further, in accordance with Hund's rule, the last two electrons in $\pi^* 2p_x$ and $\pi^* 2p_y$ orbitals will remain unpaired. Therefore, the molecule has **paramagnetic character** due to the presence of two unpaired electrons. These facts are in accordance with experimental observations. The bond dissociation energy in O_2 molecule has been found to be 498 kJ mol^{-1} and bond length 121 pm.

Comparison of O_2, O_2^+, O_2^- and O_2^{2-} species

Oxygen molecule ion (O_2^+). This ion is formed by the removal of one electron from O_2 molecule as :

$$O_2 \longrightarrow O_2^+ + e^-$$

It is clear from Fig. 61, that the electron will be lost from anti-bonding MO *i.e.* $\pi^* 2p_y$ and electronic configuration of O_2^+ is :

$$O_2^+ : KK\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^1$$

$$\text{Bond order} = \frac{8-3}{2} = \frac{5}{2} = 2\frac{1}{2}$$

Since the bond order of O_2^+ ion is greater than the bond order of O_2 molecule, therefore, the ***bond strength of O_2^+ will be more than that of O_2 molecule and bond length of O_2^+ will be less than that of O_2 molecule.***

Superoxide ion (O_2^-). This ion is formed by the addition of one electron as :

$$O_2 + e^- \longrightarrow O_2^-$$

According to Fig. 61, the electron will be added to either of the antibonding MO (*s*) ($\pi^* 2p_x$ or $\pi^* 2p_y$). The electronic configuration of O_2^- is

$$O_2^- : KK\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^2\ (\pi^* 2p_y)^1$$

$$\text{Bond order} = \frac{8-5}{2} = \frac{3}{2} = 1\frac{1}{2}$$

Since the bond order of O_2^- ion is less than that of O_2 molecule, therefore, **the bond in O_2^- will be weaker than in O_2 and bond length of O_2^- will be larger than that of O_2 molecule.**

Peroxide ion (O_2^{2-}). This ion is formed by the addition of two electrons to O_2 molecule.

$$O_2 + 2e^- \longrightarrow O_2^{2-}$$

The additional electrons enter the two half-filled π-anti-bonding MOs. The electronic configuration of O_2^{2-} ion is :

$$O_2^{2-} : KK\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^2\ (\pi^* 2p_y)^2$$

$$\text{Bond order} = \frac{8-6}{2} = 1$$

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Since bond order of O_2^{2-} ion is less than that of O_2 molecule, therefore, ***the bond O_2^{2-} will be weaker than in O_2 and bond length of O_2^{2-} will be larger than that of O_2 molecule.***

The experimental bond dissociation energies and bond lengths for O_2, O_2^+ and O_2^- are given below :

Species	Bond order	Bond dissociation energy (kJ mol^{-1})	Bond length
O_2^+	$2\frac{1}{2}$	625	112 pm
O_2	2	495	121 pm
O_2^-	$1\frac{1}{2}$	395	130 pm

The species O_2, O_2^+, O_2^- and O_2^{2-} can be arranged as:
Bond dissociation energy : $O_2^+ > O_2 > O_2^- > O_2^{2-}$
Bond length : $O_2^{2-} > O_2^- > O_2 > O_2^+$

11. Fluorine molecule (F_2). The electronic configuration of fluorine atom is $1s^2\ 2s^2\ 2p^5$ and therefore, there are 14 electrons in the valence shell of F_2 molecule. The molecular orbital electronic configuration of the molecule is :

$F_2 : KK\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^*2p_x)^2\,(\pi^*2p_y)^2$

$$\text{Bond order} = \frac{8-6}{2} = 1.$$

Thus, there is one **σ-bond** in the molecule. Since all the electrons in the molecular orbitals are paired, it is **diamagnetic.** The single bond in the molecule is also in agreement with bond dissociation energy of 159 kJ mol^{-1} and bond length equal to 143 pm.

12. Hypothetical neon molecule. The electronic configuration of neon atom is $1s^2\ 2s^2\ 2p^6$ and the molecular orbital electronic configuration of neon molecule is

$F_2 : KK\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^*2p_x)^2\,(\pi^*2p_y)^2\,(\sigma^*2p_z)^2$

$$\text{Bond order} = \frac{8-8}{2} = 0.$$

Thus, Ne_2 molecule **does not exist.**

SOLVED EXAMPLES

Example 16. *Arrange the following species in the decreasing order of their bond dissociation enthalpies :*

O_2, O_2^+ and O_2^-.

Solution : The bond dissociation enthalpy of a molecule is related to its bond order. The larger the bond order, the greater will be the bond dissociation enthalpy. We shall first calculate the bond orders for the various species from their electronic configurations.

$O_2 : KK\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^*2p_x)^1\,(\pi^*2p_y)^1$

$$\therefore \quad \text{Bond order} = \frac{8-4}{2} = 2.$$

$O_2^+ : KK\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^*2p_x)^1$

$$\therefore \quad \text{Bond order} = \frac{8-3}{2} = 2\frac{1}{2}$$

$O_2^- : KK\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^*2p_x)^2\,(\pi^*2p_y)^1$

$$\therefore \quad \text{Bond order} = \frac{8-5}{2} = 1\frac{1}{2}$$

Now, O_2^+ has the highest bond order, it will have largest bond dissociation enthalpy. The bond dissociation enthalpies will decrease in the order $O_2^+ > O_2 > O_2^-$.

Example 17. *With the help of M.O. theory, predict which of the following species is diamagnetic : H_2^+, O_2, O_2^{2+}*

Solution : The diamagnetic species are those which contain only paired electrons. This can be predicted from the molecular orbital electronic configurations as given below :

H_2^+ : $(\sigma 1s)^1$

O_2 : $KK\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^*2p_x)^1\,(\pi^*2p_y)^1$

O_2^{2+} : $KK\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2$

Since O_2^{2+} contain all paired electrons, it will be diamagnetic.

Example 18. *Explain why N_2 has greater bond dissociation energy than N_2^+ whereas O_2 has lesser bond dissociation energy than O_2^+.*

Solution: The M.O. electronic configurations are :

N_2 : $KK(\sigma 2s)^2\,(\sigma^*2s)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\sigma 2p_z)^2$

$$\text{Bond order} = \frac{8-2}{2} = 3$$

N_2^+ : $KK\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\sigma 2p_z)^1$

$$\text{Bond order} = \frac{7-2}{2} = 2\frac{1}{2}$$

Since bond order of N_2 is larger than that of N_2^+, N_2 has greater bond dissociation energy than N_2^+.

O_2 : $KK(\sigma 2s)^2\,(\sigma^*2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^*2p_x)^1\,(\pi^*2p_y)^1$

$$\text{Bond order} : \frac{8-4}{2} = 2$$

O_2^+ : $KK\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^*2p_x)^1$

$$\text{Bond order} = \frac{8-3}{2} = 2\frac{1}{2}$$

Since bond order of O_2 is less than that of O_2^+, O_2 has lower bond dissociation energy than O_2^+.

Example 19. *Which of the two : peroxide ion or superoxide ion has larger bond length ?*

Solution: The bond length of a molecule is related to its bond order. The larger the bond order, the smaller will be the bond length.

Superoxide ion, O_2^-:

$O_2^- : KK\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^*2p_x)^2\,(\pi^*2p_y)^1$

$$\text{Bond order} = \frac{8-5}{2} = 1\frac{1}{2}$$

Peroxide ion, O_2^{2-}:

$O_2^{2-} : KK(\sigma 2s)^2\,(\sigma^*2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^*2p_x)^2\,(\pi^*2p_y)^2$

$$\text{Bond order} = \frac{8-6}{2} = 1$$

Now, superoxide ion (O_2^-) has larger bond order than peroxide ion (O_2^{2-}), therefore, bond length of peroxide ion will be larger.

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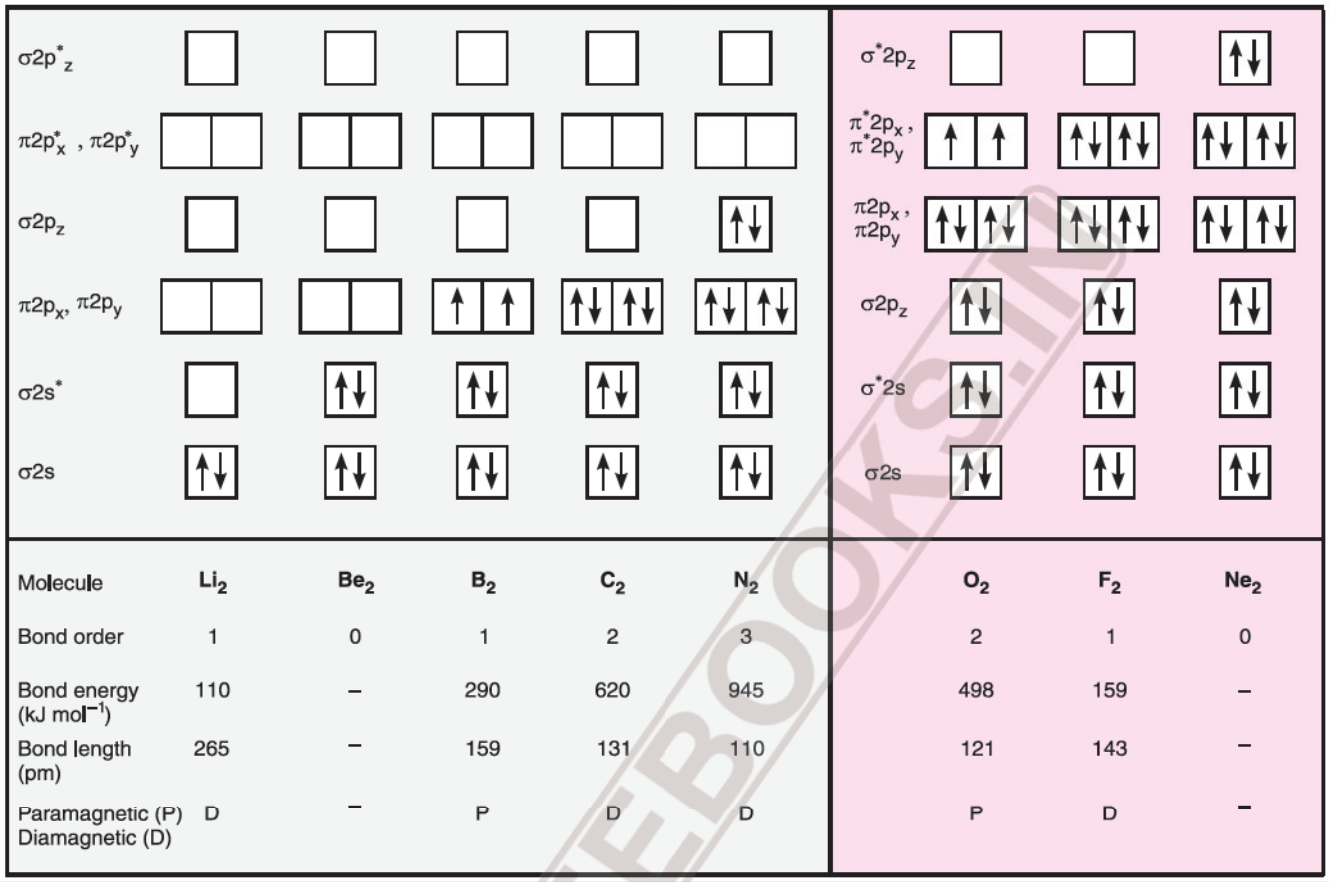
SUM UP

M.O. occupancy and molecular properties of homonuclear diatomic molecules of second period.



Molecule	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	0	1	2	3	2	1	0
Bond energy (kJ mol^{-1})	110	–	290	620	945	498	159	–
Bond length (pm)	265	–	159	131	110	121	143	–
Paramagnetic (P) Diamagnetic (D)	D	–	P	D	D	P	D	–

MOLECULAR ORBITAL ELECTRONIC CONFIGURATIONS OF SOME COMMON HETERONUCLEAR MOLECULES

The configurations of heteronuclear molecules (containing different atoms) can be written in a similar manner as in case of homonuclear molecules.

(*i*) NO : Total number of electrons = 7 + 8 = 15

NO : $KK(\sigma 2s)^2(\sigma^*2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2(\pi^*2p_x)^1$

Bond order = $\frac{8-3}{2} = 2\frac{1}{2}$

(*ii*) NO^+ : $KK\ (\sigma 2s)^2\ (\sigma^*2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2$

Bond order = $\frac{8-2}{2} = 3$

(*iii*) **CN :** Total number of electrons = 6 + 7 = 13

CN : $KK\ (\sigma 2s)^2\ (\sigma^*2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^1$

Bond order = $\frac{7-2}{2} = 2\frac{1}{2}$

(*iv*) CN^- : $KK\ (\sigma 2s)^2\ (\sigma^*2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2$

Bond order = $\frac{8-2}{2} = 3$

(*v*) **CO** : Total number of electrons = 6 + 8 = 14

CO : $KK\ (\sigma 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2\ (\sigma^*2s)^2$

Bond order = $\frac{8-2}{2} = 3$

Summary of MO electronic configurations for some heteronuclear diatomic molecules.

Valence electrons	Species	MO electronic configuration	Bond order	Bond dissociation energy (kJ mol^{-1})	Bond length (Å)
8	BN	$KK(\sigma 2s)^2\ (\sigma^*2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2$	2	385	128 pm
9	BO	$KK(\sigma 2s)^2\ (\sigma^*2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2(\sigma 2p_z)^1$	$2\frac{1}{2}$	773	120 pm
	CN			786	117 pm
	*CO^+				111 pm
10	*CO	$KK(\sigma 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2(\sigma 2p_z)^2\ (\sigma^*2s)^2$	3	1067	113 pm
	NO^+				106 pm
11	NO	$KK(\sigma 2s)^2\ (\sigma^*2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2\ (\pi^*2p_x)^1$	$2\frac{1}{2}$	667	115 pm

* It may be noted that in CO and CO^+, σ^*2s MO is higher in energy than $\pi 2p_x$, $\pi 2p_y$ and $\sigma 2p_z$ MOs and the configurations are, CO : $KK(\sigma\ 2s)^2\ (\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2(\sigma^*2s)^2$ and CO^+ : $KK(\sigma 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2(\sigma^*2s)^1$

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Practice Problems

- **20.** Which of the two : O_2^{2+} or O_2^{2-} is more stable ?
- **21.** Arrange the following in the increasing order of bond length : O_2, O_2^-, O_2^+
- **22.** Calculate the bond order in
  (*i*) H_2^+ (*ii*) H_2^- (*iii*) He_2^+ (*iv*) O_2^+
- **23.** Which two of H_2^+, H_2^- and H_2^{2-} have the same bond order ?
- **24.** Compare bond order in N_2 and N_2^+.
- **25.** Calculate the bond order of He_2^+ molecular ion.
- **26.** Write which out of O_2^+ and O_2^- is more stable.
- **27.** Indicate which one from O_2^- and O_2^{2-} may exhibit paramagnetism ?

Answers to Practice Problems

- **20.** O_2^{2+}
- **21.** $O_2^+ < O_2 < O_2^-$
- **22.** (*i*) $\frac{1}{2}$ (*ii*) $\frac{1}{2}$ (*iii*) $\frac{1}{2}$ (*iv*) $2\frac{1}{2}$
- **23.** H_2^+ and H_2^-
- **24.** Bond order in $N_2 = 3$, $N_2^+ = 2\frac{1}{2}$
- **25.** $\frac{1}{2}$ **26.** O_2^+ **27.** O_2^-

HYDROGEN BONDING

When hydrogen atom is bonded to atoms of highly electronegative elements such as fluorine, oxygen or nitrogen, the hydrogen atom forms a weak bond with the electronegative atom of the other molecule. This weak bond is called **hydrogen bond.** For example, in hydrogen fluoride, HF, hydrogen atom forms a weak bond with fluorine atom of the neighbouring molecule, while remaining bonded to its fluorine atom. This may be shown as :

H — F ····· H — F ····· H — F

In other words, hydrogen atom acts as a bridge between two atoms, holding one atom by a covalent bond and the other atom by a hydrogen bond. The hydrogen bond is represented by dotted line (.....) while the covalent bond is represented by solid line (—). As a result of hydrogen bonding, HF exists as a cluster of hydrogen fluoride molecules and is represented as $(HF)_n$. Thus,

the attractive force which binds hydrogen atom of one molecule with electronegative atom (F, O or N) of another molecule is known as hydrogen bond or hydrogen bonding.

Strength of hydrogen bond. Hydrogen bond is much weaker than a covalent bond. The strength of hydrogen bond ranges from 10–40 kJ mol^{-1} while that of a normal covalent bond is of the order of 400 kJ mol^{-1}. Thus, a hydrogen bond is about one-tenth of the strength of a covalent bond. It may also be noted that the bond length of a hydrogen bond is larger than that of a covalent bond. For example, in case of HF molecule, the covalent bond between H and F is 109 pm while the bond length of hydrogen bond between F and H is 155 pm.

Cause of formation of hydrogen bond. When hydrogen is bonded to strongly electronegative element, A (such as F, O or N) the electron pair shared between the two atoms lies far away from the hydrogen atom. As a result, hydrogen atom becomes highly electropositive with respect to the other atom, A. Since the electrons are displaced towards A, it acquires partial negative charge (δ–) while hydrogen atom gets partial positive charge (δ+).

In other words, the bond H—A becomes polar and may be represented as $H^{\delta+}$—$A^{\delta-}$. The electrostatic force of attraction between positively charged hydrogen atom of one molecule and negatively charged atom of neighbouring molecule results in the formation of hydrogen bond. This may be represented as :

$$\cdots\overset{\delta+}{H}\!\!-\!\!\overset{\delta-}{A}\cdots\cdots\overset{\delta+}{H}\!\!-\!\!\overset{\delta-}{A}\cdots\cdots\overset{\delta+}{H}\!\!-\!\!\overset{\delta-}{A}\cdots$$

Conditions for Hydrogen Bonding

The following conditions are necessary for the formation of hydrogen bonding :

(*i*) **High electronegativity of atom bonded to hydrogen.** The molecule should contain an atom of high electronegativity such as F, O or N bonded to hydrogen atom. The common examples are HF, H_2O and NH_3.

(*ii*) **Small size of the electronegative atom.** The size of the electronegative atom should be quite small. This is due to the fact that the smaller the size of electronegative atom, the greater will be its attraction for the bonded electron pair. This will cause greater polarity in the bond between H and electronegative atom which results in stronger hydrogen bond. For example, NH_3 shows hydrogen bonding while HCl does not, although both N and Cl have the same electronegativity (3.0). Hydrogen bonds are not formed by Cl because of its bigger size than nitrogen.

Differences between hydrogen bond and covalent bond.

The main points of differences between hydrogen bond and covalent bond are :

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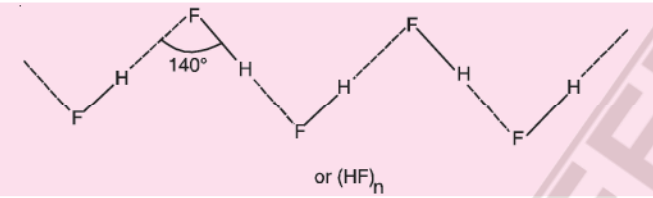
Hydrogen bond	Covalent bond
1. Hydrogen bond involves dipole-dipole attractions.	1. Covalent bond involves sharing of electrons.
2. It is formed between hydrogen atom and a highly electronegative atom (F, O or N).	2. It is formed between any two electronegative atoms which may be of the same element or of different elements.
3. Strength of hydrogen bond is very small *e.g.* bond strength of H ..... F bond is 41.83 kJ mol^{-1}.	3. Bond strength of covalent bond is sufficiently high. For example, bond strength of H–H bond is 433 kJ mol^{-1}.

Examples of Hydrogen Bonded Compounds

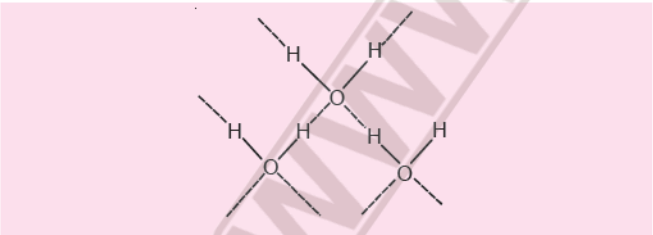
A few examples of compounds which exhibit hydrogen bonding are discussed below :

1. Hydrogen fluoride. In the solid state, hydrogen fluoride consists of long zig-zag chains of molecules associated together through hydrogen bonds. Thus, hydrogen fluoride molecule is represented as $(HF)_n$. In the liquid or gaseous state, the chain however, becomes linear.



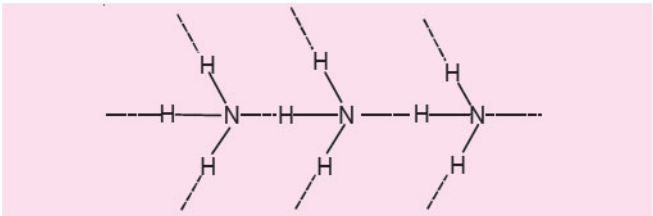
or $(HF)_n$

2. Water. Hydrogen bonding exists in water molecules also. In addition to two covalent (O—H) bonds in water, oxygen atom forms two hydrogen bonds. As a result of hydrogen bonds, each oxygen is tetrahedrally surrounded by four hydrogen atoms, two by covalent bonds and two by hydrogen bonds.



The associated water molecules may be expressed as $(H_2O)_n$.

3. Ammonia. Ammonia molecule has an electronegative nitrogen atom bonded to three hydrogen atoms. Due to difference in electronegativity between nitrogen and hydrogen, each hydrogen atom acquires positive charge. Thus, in the molecule, there is one negative site and three positive sites so that the molecules of ammonia associate through hydrogen bonding to form long chains.



Types of Hydrogen Bonds

Hydrogen bonds can be classified into two types :

(*a*) *Intermolecular hydrogen bond.*

(*b*) *Intramolecular hydrogen bond.*

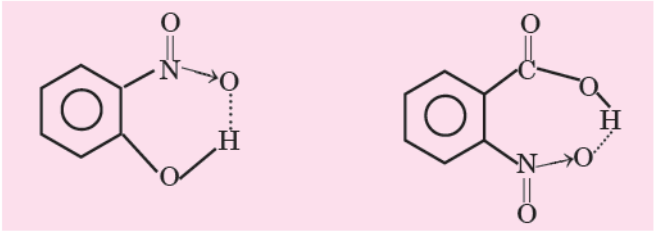
(*a*) Intermolecular hydrogen bond. Intermolecular hydrogen bond is formed between two different molecules of the same or different substances. For example,

(*i*) *hydrogen bond between the molecules of hydrogen fluoride.*

(*ii*) *hydrogen bond in alcohol or water molecules.*

Intermolecular hydrogen bond results into association of molecules. Hence, it usually increases the melting point, boiling point, viscosity, surface tension, solubility, etc.

(*b*) Intramolecular hydrogen bond. *Intramolecular hydrogen bond is formed between the hydrogen atom and the highly electronegative atom (F, O or N) present in the same molecule.* Intramolecular hydrogen bond results in the cyclisation of the molecules and prevents their association. Consequently, the effect of intramolecular hydrogen bond on the physical properties is negligible.



Ortho nitrophenol Ortho nitrobenzoic acid

For example, intramolecular hydrogen bonds are present in molecules such as *o*-nitrophenol, *o*-nitrobenzoic acid, etc.

Influence of Hydrogen Bonding on the Properties

Hydrogen bonding has important effect on many physical properties such as melting point, boiling point and solubility of the compounds. The main characteristics of compounds having hydrogen bonds are given below :

1.Association. Due to intermolecular hydrogen bonding, two or more molecules of a compound exist as associated molecules. For example, carboxylic acids (RCOOH) exist as dimers even in the vapour state as shown ahead :

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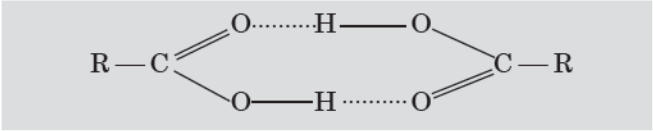

This results in the increase in the size as well as in the molecular mass of the compound.

2. Higher melting and boiling points. The compounds containing hydrogen bonds have high melting and boiling points. It is due to the fact that because of hydrogen bonding, the electrostatic force of attraction in the molecules become large. Consequently, larger energy is required to separate these molecules before they can melt or boil. The influence of hydrogen bonding on melting and boiling points can be understood comparing the melting and boiling points of the hydrides of elements of groups 14, 15, 16 and 17 (Table 11).

Table 11. Melting and boiling points (K) of hydrides of groups 14, 15, 16 and 17.

Hydride	m.p.	b.p.
	Group 14	
CH_4	89.0	111.5
SiH_4	88.0	161.2
GeH_4	108.0	183.0
SnH_4	123.0	221.0
	Group 15	
NH_3	195.5	239.6
PH_3	138.0	185.0
AsH_3	159.0	218.0
SbH_3	184.0	256.0
	Group 16	
H_2O	273.0	373.0
H_2S	190.3	211.2
H_2Se	209.0	231.0
H_2Te	222.0	271.0
	Group 17	
HF	180.7	292.4
HCl	161.0	189.4
HBr	184.5	206.0
HI	222.2	237.0

The melting points and boiling points of hydrides of elements of these groups are also plotted against their molecular masses in Fig. 62(a) and 62(b). It is clear from Table 12. that the melting and boiling points increase as the molecular mass increases in group 14. This is mainly due to the fact that as the size of elements of group 14 increases, the number of electrons also increases. As a result, van der Waals' forces also increase and therefore, melting and boiling points increase. However, hydrides of groups 15, 16 and 17 do not show this trend. In these groups, the melting and boiling points also increase with increasing molecular mass with the exception of first member. But, the first members NH_3 (group 15), H_2O (group 16) and HF (group 17) have abnormally high melting and boiling points. The relatively high melting and boiling points of the first member of each group is due to the intermolecular hydrogen bonding shown by these compounds. For example, the boiling point of HF is much more than that of HCl due to larger hydrogen bonding in the former. Similarly, we can account for the higher values of boiling points of NH_3 and H_2O in their groups.

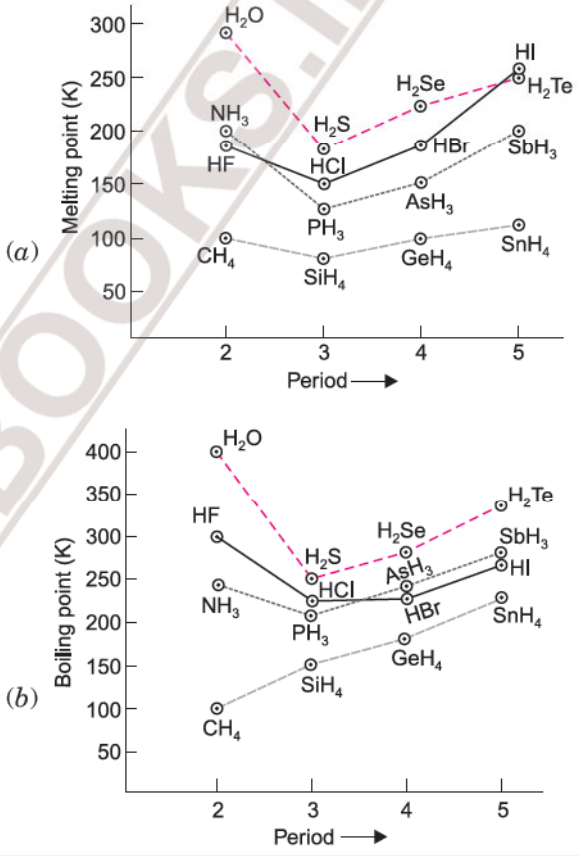

Fig. 62. (a) Melting points (b) Boiling points of hydrides of groups 14, 15, 16 and 17.

It is interesting to note that hydrogen bond in HF is stronger than in H_2O. However, water boils at a higher temperature than HF. This is due to the reason that each H_2O molecule is bonded to four other H_2O molecules (discussed later) through hydrogen bonds whereas each HF molecule is bonded to two other HF molecules through hydrogen bonds.

3. Influence on the physical state. Hydrogen bonding also influences the physical state of the substances (solid, liquid or gas). For example, both O and S belong to same group but H_2O is a liquid at ordinary temperature, while H_2S is a gas. This is explained on the basis of electronegativity values.

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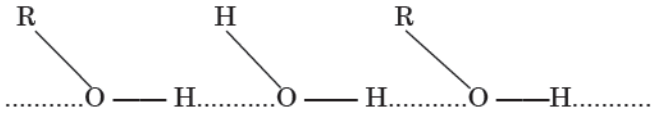
H_2O molecule	*H_2S molecule*
Electronegativity of O = 3.5	Electronegativity of S = 2.5
Electronegativity of H = 2.1	Electronegativity of H = 2.1

In water, oxygen is highly electronegative so that it forms hydrogen bonds. As a result, the molecules of H_2O get associated with one another and this raises the boiling point of water. Consequently, water exists as liquid at room temperature. On the other hand, the electronegativity difference of atoms in H_2S is less and hydrogen bonding in H_2S is almost negligible. As a result, H_2S is not associated and exists as a gas at room temperature.

4. Solubility. Hydrogen bonding also influences the solubility of one substance in another. For example, alcohol is highly soluble in water due to hydrogen bonding with water molecules as shown below :



5. Volatility. The compounds involving hydrogen bonding between different molecules such as NH_3, H_2O and HF have higher boiling points. Therefore, they are less volatile as compound to the other corresponding members of their groups. The enthalpies of vaporisation follows almost the same pattern as shown by their melting points and boiling points [Fig. 62(*a*) and (*b*)]. For example, in group 17, the enthalpies of vaporisation decrease in the order.

$HCl < HBr < HI < HF$

Similarly, in groups 15 and 16 the trends are :

$H_2S < H_2Se < H_2Te < H_2O$

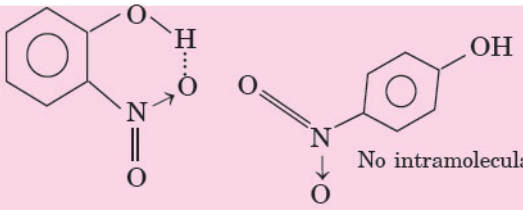
$PH_3 < AsH_3 < SbH_3 < NH_3$

Practice Problems

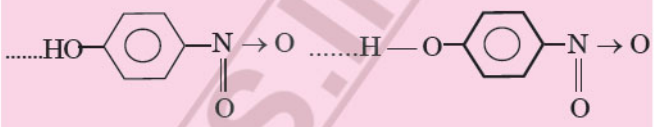
- **29.** Arrange the following in the decreasing order of their boiling points HF, HCl, HBr
- **30.** Do *o*-nitrophenol and *p*-nitrophenol have hydrogen bonding in their molecules? Explain which of the two has higher boiling point?

Answers to Practice Problems

- **29.** HF > HBr > HCl.
- **30.** Both have hydrogen bonding. *o*-Nitrophenol has **intramolecular** hydrogen bonds. But due to larger distance between —NO_2 and —OH groups in *p*-nitrophenol, there is no such bonding.



However, there is intermolecular hydrogen bonding in *p*-nitrophenol and therefore, it exists as associated molecule. In *o*-nitrophenol, no intermolecular hydrogen bonding is possible.



Due to associated nature of *p*-nitrophenol, it is less volatile and has high boiling point.

Water an unusual Liquid

Water is the most common substance on the earth's surface. It has many unusual properties. One of the most important of these is its ability to dissolve a variety of compounds. It dissolves many ionic compounds, many polar inorganic and organic compounds. In addition, water has high heat of vaporisation, high heat of fusion, high specific heat, good liquid range (from 0°C freezing point to 100°C boiling point).

Water has interesting structure and this accounts for its many unusual properties. These can be explained on the basis of hydrogen bonding.

Hydrogen bonding in water and ice

The phenomenon of hydrogen bonding is responsible for the interesting behaviour of water. It is a common observation that density of ice is less than that of water because ice always floats over water. Moreover, it is a well known fact that density of water is maximum at 4°C. Let us explain these observations :

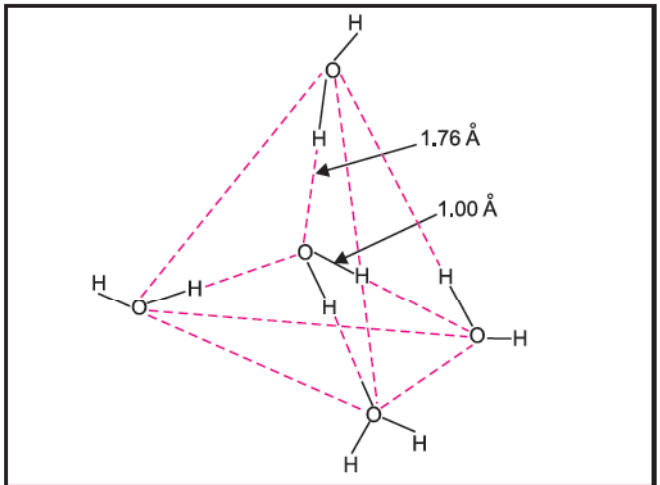


Fig. 63. Tetrahedral arrangement of water molecules.

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(*i*) Ice is lighter than water.

X-ray studies have shown that in ice, each oxygen atom is tetrahedrally surrounded by four hydrogen atoms in such a way that two hydrogen atoms are linked to oxygen atom by covalent bonds. These hydrogen atoms lie closer to the oxygen atom at a distance of 1.00 Å. The other two hydrogen atoms are linked to the central oxygen atom by hydrogen bonds. They lie away from oxygen atom at a distance of 1.76Å. The oxygen atoms of water molecules are located at the corners of tetrahedron. This arrangement is shown in Fig. 64.

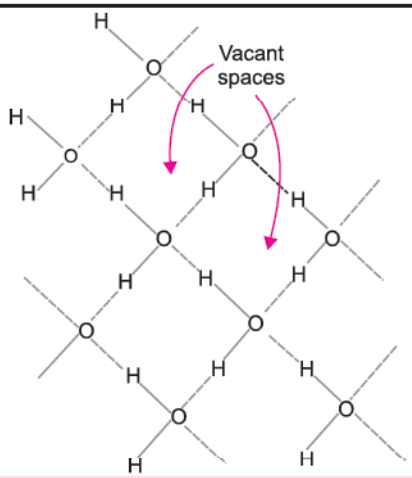

Fig. 64. Open cage like structure of ice.

As a result of tetrahedral arrangement of H_2O molecules in the solid state, the ice structure extends in three dimensions. Since hydrogen bonds between oxygen and H atoms are longer than the covalent bonds between them, the molecules of H_2O are not packed closely, but there are *vacant spaces* present in the crystal structure. This gives rise to an open cage like structure for ice having a larger volume for the given mass of water. Consequently, the density of ice is less than water.

(*ii*) Water has maximum density at 4°C.

When ice is melted by increasing its temperature, the open cage structure starts collapsing due to partial break down of the hydrogen bonds. This allows H_2O molecules to come closer and also the water molecules separated from ice structure fill the vacant spaces in open-cage structure. This results into concentration of volume. Hence, the density of water starts increasing on heating above the melting point of ice and becomes maximum at 4°C. On further rise in temperature, the kinetic energy of molecules increases and they once again start moving away from one another. This causes expansion which is much more than the concentration caused by breaking of hydrogen bonds. Therefore, above 4°C the density of water once again starts decreasing. Thus, the maximum density of water is at 4°C.

add on Conceptual Questions 3

CONCEPTUAL QA

Q. 1. In going from O_2 to O_2^+, the bond dissociation energy increases and bond length decreases. Do we expect the same behaviour for the change N_2 to N_2^+ ?

Ans. On going from $O_2 \longrightarrow O_2^+ + e^-$

bond order increases from 2 to 2.5 because the electron is lost from antibonding MO. Therefore, its bond dissociation energy increases but bond length decreases because bond order is directly proportional to bond dissociation energy but inversely proportional to bond length.

However, on going from

$N_2 \longrightarrow N_2^+ + e^-$

electron is lost from bonding MO and the bond order decreases from 3 to 2.5. Therefore, the bond dissociation energy decreases and the bond length increases.

Q. 2. Which of the two : O_2^- or O_2^{2-} has higher bond order and why ?

Ans. O_2^- has higher bond order (1.5) than O_2^{2-} (1.0) because O_2^- has lesser number of electrons in antibonding MOs.

Q. 3. Why is the energy of $\pi 2p_x$ and $\pi 2p_y$ MOs lower than $\sigma 2p_z$ MO in N_2 molecule ?

Ans. This is because of intermixing of $2s$ and $2p_z$ orbitals because of their close proximity. Due to intermixing $\sigma 2p_z$ MO becomes higher in energy than $\pi 2p_x$ and $\pi 2p_y$ MOs.

Q. 4. Write which one out of O_2^+ and O_2^- is more stable on the basis of bond order calculations.

Ans. Bond order in O_2^+ is 2.5 and in O_2^- is 1.5. Therefore, O_2^+ is more stable.

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Q. 5. Use molecular orbital theory to explain why the Be_2 molecule does not exist. *N.C.E.R.T.*

Ans. M.O. energy level configuration for Be_2 molecule is

Be_2 : KK $(\sigma 2s)^2 (\sigma^* 2s)^2$ Bond order = $\frac{2-2}{2} = 0$

Since bond order of Be_2 molecule is zero, this means that Be_2 molecule does not exist.

Q. 6. Compare the relative stability of the following species and indicate their magnetic properties: O_2, O_2^+, O_2^- (superoxide), O_2^{2-} (peroxide). *N.C.E.R.T.*

Ans. The stability can be decided on the basis of bond order as :

O_2 : KK $(\sigma 2s)^2(\sigma 2s^*)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1(\pi^* 2p_y)^1$ Bond order = $\frac{8-4}{2} = 2$ Paramagnetic

O_2^+ : KK $(\sigma 2s)^2(\sigma 2s^*)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1$ Bond order = $\frac{8-3}{2} = 2.5$ Paramagnetic

O_2^- : KK $(\sigma 2s)^2(\sigma 2s^*)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^1$ Bond order = $\frac{8-5}{2} = 1.5$ Paramagnetic

O_2^{2-} : KK $(\sigma 2s)^2(\sigma 2s^*)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^2$ Bond order = $\frac{8-6}{2} = 1$ Diamagnetic

Larger the bond order greater is the stability, So the stability decreases as : $O_2^+ > O_2 > O_2^- > O_2^{2-}$

CONCEPTUAL QA

Q. 7. What is the effect of the following processes on the bond order of N_2 and O_2 ?

(a) $N_2 \longrightarrow N_2^+ + e^-$ **(b)** $O_2 \longrightarrow O_2^+ + e^-$

Ans. (*a*) Bond order decreases from 3 to 2.5

(*b*) Bond order increases from 2 to 2.5

Q. 8. List two main conditions for forming hydrogen bonds.

Ans. (*i*) High electronegativity of atom bonded to hydrogen.

(*ii*) Small size of the electronegative atom.

Q. 9. Why does formic acid exist as dimer ? What is its one consequence ?

Ans. Formic acid exists as dimer because of hydrogen bonding.

Because of hydrogen bonding, it has larger size as well as molecular mass.

Q. 10. Select the molecule in each of the following having higher property mentioned :

(*i*) F .....H–F, F–H.....O : stronger hydrogen bond

(*ii*) CH_4, SiH_4 : boiling point

(*iii*) HF, HCl : boiling point

(*iv*) Ice, water : density

Ans. (*i*) F.....H–F (*ii*) SiH_4 (*iii*) HF (*iv*) water.

Q. 11. How can one non-polar molecule induce a dipole in a nearby non-polar molecule ? *N.C.E.R.T.*

Ans. In a non-polar molecule, there may be instantaneous dipole created by specific positions of electrons. This instantaneous dipole can induce a dipole in a nearby non-polar molecule.

Q. 12. Considering *z*-axis as the internuclear axis, which of the following will not form sigma bond ?

(*a*) 2*s* and 2*s* (*b*) $2p_y$ and $2p_y$ (*c*) 2*s* and $2p_z$ (*d*) $2p_x$ and $2p_z$ (*e*) $2p_z$ and $2p_z$.

Ans. (*b*) and (*d*).

Q. 13. Which of the following substances exhibit hydrogen bonding? Draw the hydrogen bonds between two molecules of the substance where appropriate :

(*i*) CH_3CH_2OH **(*ii*)** $CH_3\overset{\overset{O}{\|}}{C}-CH_3$ **(*iii*)** $CH_3-\overset{\overset{O}{\|}}{C}-OH$ **(*iv*)** $CH_3-\overset{\overset{O}{\|}}{C}-NH_2$ *N.C.E.R.T.*

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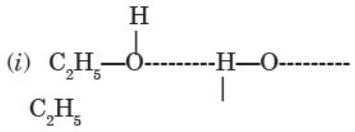
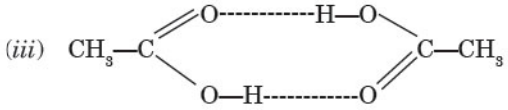
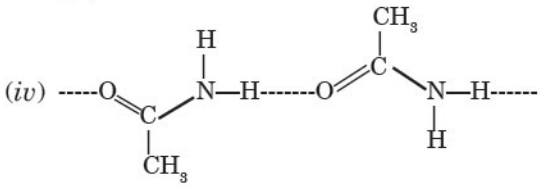
Ans. (*i*), (*iii*) and (*iv*) exhibit hydrogen bonding.







Chapter Summary

Key Terms

- **Chemical bond.** The attractive force which holds together the constituent particles (atoms, ions or molecules) in a chemical specie.
- **Ionic bond or electrovalent bond.** The electrostatic force which holds the oppositely charged ions together.
- **Electrovalency.** The number of electrons which an atom loses or gains.
- **Covalent bond.** The bond formed by mutual sharing of electrons between combining atoms of the same or different elements.
- **Coordinate bond.** A covalent bond in which both the electrons in the shared pair come from one atom.
- **Lattice enthalpy.** The amount of energy released when one mole of ionic crystal is formed from its constituent ions in gaseous state.
- **Dipole moment.** A vector quantity defined as the product of charge developed on any of the atom in a bond and distance between the atoms.
- **Hybridisation.** The phenomenon of intermixing of the orbitals of slightly different energies so as to redistribute their energies and to give new set of orbitals of equivalent energies and shape.
- **Resonance.** When a molecule cannot be represented by a single structure but its characteristic properties can be described by two or more than two structures, then the actual structure is said to be resonance hybrid of these structures. This phenomenon is called **resonance.** The various contributing structures are called **resonating structures.**
- **Canonical form.** The contributing structures taken together contribute the resonance hybrid which represents the molecule or ion.
- **Resonance energy.** The difference between the actual bond energy and the most stable of the resonating structures.

QUICK CHAPTER ROUND UP

CHEMICAL BONDS

Ionic Bond
formed by transfer of electrons from one atom to other

- The ionisation enthalpy of atom forming the cation should be low.
- The electron gain enthalpy of atom forming the anion should be highly negative.
- Lattice enthalpy should be high.

Covalent Bond
formed by sharing of electrons between atoms

- Each atom may contribute one or more electrons for sharing
- Atoms attain stable noble gas configurations.

Coordinate Bond
covalent bond in which both the electrons in the shared pair come from one atom.

- One of the atoms or group of atoms is deficient of two electrons
- Other atom has stable noble gas configuration

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Lattice Enthalpy depends upon
- **Size of ions.** Smaller the size of ion, higher is lattice enthalpy
- **Charge on ions.** Greater the charge on ions, higher is lattice enthalpy

➤ LiF > NaF > KF > RbF ; $AlCl_3 > BaCl_2 > NaCl$

Exceptions to Octet rule
- Incomplete octet

  H : Be : H , F : B(F) : F
- Expanded octet

  PF_5, SF_6, IF_7
- Odd electron molecules

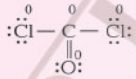
  ·N=O: (Nitric oxide) ; O=N–O: (Nitrogen dioxide)

FORMAL CHARGE

Formal charge on an atom =

$$\left(\begin{matrix}\text{Total number of}\\ \text{valence electrons}\\ \text{in free atom}\end{matrix}\right) - \left(\begin{matrix}\text{Total number of}\\ \text{non-bonding}\\ \text{(lone pair) electrons}\end{matrix}\right) - \frac{1}{2}\left(\begin{matrix}\text{Total number of}\\ \text{bonding}\\ \text{(shared) electrons}\end{matrix}\right)$$

or $FC = V - L - \frac{1}{2}S$

e.g., 

RESONANCE STRUCTURES

Dipole Moment

The product of the magnitude of the charge and the distance of separation between the charges

$\mu = q \times d$

Units: **Debye**

$1D = 1 \times 10^{-18}$ esu.cm

% Ionic character =

$$\frac{\text{Observed dipole moment}}{\text{Dipole moment for complete ionic character}} \times 100$$

➤ If electronegativity difference (ΔEN) is 1.7

⇒ 50% ionic & 50% covalent

ΔEN > 1.7 ⇒ ionic

ΔEN < 1.7 ⇒ covalent

Symmetrical molecules ⇒ Non-polar

CO_2 , BF_3, BeF_2, CH_4

Unsymmetrical molecules ⇒ Polar

H_2O , NH_3, $CHCl_3$

NH_3 ⇒ 1.47 D

NF_3 ⇒ 0.24D

- Fajan's rules

  Covalent character will be favoured by
  - (*i*) Small size of cation
  - (*ii*) Large size of anion
  - (*iii*) High charge of cation and anion
  - (*iv*) The cation having 18-electrons shell.

According to **quantum theory of covalent bond**, *the bond is formed by the overlapping of half filled atomic orbitals having electrons with opposite spins. The greater the overlapping, the stronger is the bond formed between two atoms.*

The relative arrangement of the bonded atoms in a molecule is called **geometry of the molecule.**

VSEPR THEORY

helps to predict the shapes/geometries of molecules. Shapes are predicted from number of electron pairs

Lone pair-Lone pair > Lone pair-Bond pair > Bond pair-Bond pair.

Molecules with bond pairs only

2 bond pairs ⇒ Linear
e.g., $BeCl_2$, CO_2

3 Bond pairs ⇒ trigonal planar
e.g., BF_3, $AlCl_3$

4 bond pairs ⇒ Tetrahedral
e.g., CH_4, SiF_4

5 Bond pairs ⇒ trigonal bipyramidal
e.g., PF_5, $SbCl_5$

6 Bond pairs ⇒ Octahedral
e.g., SF_6, TeF_6

7 Bond pairs ⇒ pentagonal bipyramidal
e.g., IF_7

Molecules with bond pairs and lone pairs

AB_3L
NH_3 ⇒ pyramidal

AB_2L_2
Water ⇒ V-shaped

AB_4L
SF_4 ⇒ See saw

AB_3L_2
ClF_3 ⇒ T shaped

AB_2L_3
XeF_2 ⇒ Linear

AB_5L
BrF_5 ⇒ Square pyramidal

AB_4L_2
XeF_4 ⇒ Square planar

The hybridisation also helps to know the geometry of molecules.

MOLECULAR ORBITAL THEORY
- MOs are formed by the combination of atomic orbitals of same symmetry and of nearly same energy.
- If *z*-axis is internuclear axis, $2p_z$ orbitals combine to form σ MOs while $2p_x$ and $2p_y$ can combine to form π MOs.
- 2s orbital may combine with $2p_z$ orbital but it cannot combine with $2p_x$ or $2p_y$ orbitals.
- Larger the bond order of a molecule, greater will be its bond dissociation energy and smaller will be its bond length.

Sequence of energy levels
- For molecules Li_2, Be_2, B_2, C_2, N_2

  $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \pi 2p_x = \pi 2p_y, \sigma 2p_z, \pi^* 2p_x = \pi^* 2p_y, \sigma^* 2p_z$
- For molecules O_2, F_2, Ne_2

  $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, \pi 2p_x = \pi 2p_y, \pi^* 2p_x = \pi^* 2p_y, \sigma^* 2p_z$

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Bond order $= \frac{\left[\text{No. of electrons in bonding MOs}\right] - \left[\text{No. of electrons in anti–bonding MOs}\right]}{2}$

- Larger the B.O., smaller the bond length
- Larger the B.O., greater the bond dissociation energy

$\Rightarrow$

For O_2, O_2^+, O_2^-, O_2^{2-}
Bond order
O_2^+ (2.5) > O_2(2) > O_2^- (1.5) > O_2^{2-} (1)
Bond length
$O_2^+ < O_2 < O_2^- < O_2^{2-}$
Bond dissociation energy
$O_2^+ > O_2 > O_2^- > O_2^{2-}$
Paramagnetic species $\Rightarrow$ O_2, O_2^+, O_2^-

B_2 molecule is paramagnetic because of its MO electronic configuration : KK $(\sigma 2s)^2$ $(\sigma^* 2s)^2$ $(\pi 2p_x)^1$ $(\pi 2p_y)^1$. In this case $\pi 2p_x$ and $\pi 2p_y$ MOs have lower energy than $\sigma 2p_z$ MO.

➤ Intermolecular H-bond formed between two different molecules.

➤ Intramolecular H-bond formed between H atom and electronegative atom in the same molecule.

Because of H-bonding
- Molecules have higher mpt and bpt.
- exist as associated
- Ice floats over water.

NCERT FILE Solved

NCERT Textbook Exercises

Q. 1. Explain the formation of a chemical bond.

Ans. *Refer Text page 1, 2.*

Q. 2. Write Lewis dot symbols for atoms of the following elements : Mg, Na, B, O, N, Br.

Ans. $\dot{M}g\cdot$, $\dot{N}a$, $\cdot\dot{B}\cdot$, $:\dot{O}:$, $:\dot{N}\cdot$, $:\dot{B}r\cdot$

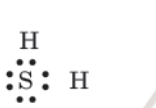
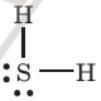
Q. 3 Write Lewis symbols for the following atoms and ions :

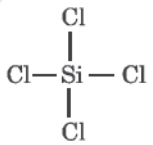
S and S^{2-}; Al and Al^{3+}; H and H^-

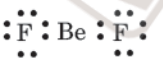
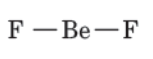
Ans. *Refer Solved Example 2. (Page 3)*

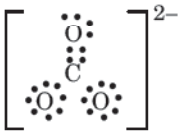
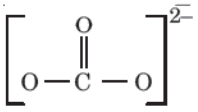
Q. 4 Draw the Lewis structures for the following molecules and ions :

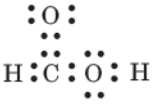
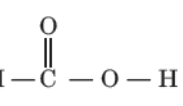
H_2S, $SiCl_4$, BeF_2, CO_3^{2-}, HCOOH

Ans. H_2S :  or 

$SiCl_4$: or 

BeF_2 :  or 

CO_3^{2-} :  or 

HCOOH :  or 

Q. 5. Define octet rule. Write its significance and limitations.

Ans. Atoms combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to complete their octets in their valence shell. This is called the octet rule.

Significance : The octet rule helps to explain as to why different atoms combine with each other to form ionic or covalent compounds.

Limitations of octet rule. *Refer exceptions to the octet rule (Page 13).*

Q. 6. Write the favourable factors for the formation of ionic bond.

Ans. The favourable factors for the formation of ionic bonds are :

(*i*) Low ionization enthalpy of the metal atom.

(*ii*) High electron gain enthalpy of the non-metal atom.

(*iii*) High lattice enthalpy of the compound formed.

Q. 7. Discuss the shape of the following molecules using the VSEPR model :

$BeCl_2$, BCl_3, $SiCl_4$, AsF_5, H_2S, PH_3

Ans. *Refer Text (Page 28, 29).*

Q. 8. Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.

Ans. NH_3 molecule has one lone pair while H_2O has two lone pairs of electrons. Due to the presence of lone pairs the geometries of NH_3 and H_2O are distorted. Due to the presence of stronger *lp–bp* repulsion

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than *bp–bp* repulsion, the bond angle in NH_3 is reduced from normal tetrahedral bond angle (109.5°) to 107°. In case of H_2O, two *lp* of electrons force the O—H bonds more closely than N–H bonds in NH_3. So the bond angle decreases to a larger extent *i.e.*, to 104.5°.

Q. 9. How do you express the bond length in terms of bond order ?

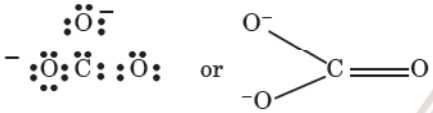
Ans. Greater the bond order, smaller is the bond length.

Q. 10. Define bond length.

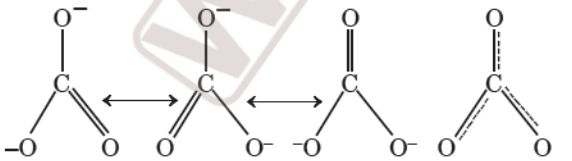
Ans. Bond length is defined as the average distance between the centres of the nuclei of two bonded atoms in a molecule. In other words, it represents the equilibrium internuclear separation distance of the bonded atoms in a molecule.

Q. 11. Explain the important aspects of resonance with reference to the CO_3^{2-} ion.

Ans. When a molecule cannot be represented by a single structure but its characteristic properties can be described by two or more than two structures, then the actual structure is said to be a resonance hybrid of these structures. For example, the carbonate ion may be represented as :

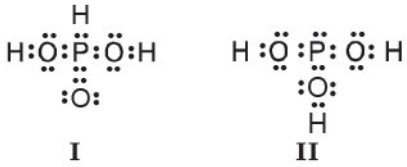


In this case, each atom has an octet of electrons. According to this structure, there are single bonds between two carbon—oxygen atoms and one double bond between carbon and oxygen atoms. Therefore, the two C—O bonds should be different than the third C=O bond. However, experimentally, it is observed that all the three bond lengths are equal and the bonds are intermediate between single and double bonds. This means that the above Lewis structure does not account for the observed experimental facts. To solve the problem, the CO_3^{2-} may be represented as resonance hybrid of the following structures.



Resonance hybrid

Q. 12. H_3PO_3 can be represented by structures 1 and II shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing H_3PO_3 ? If not, give reasons for the same.

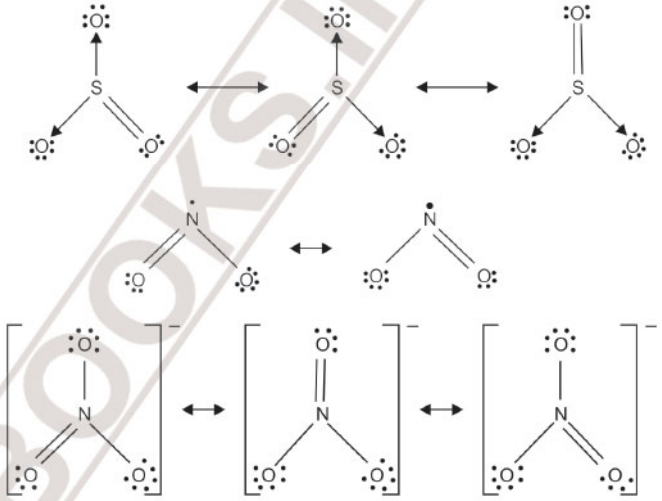


I II

Ans. No, these cannot be taken as canonical forms because the position of atoms have changed.

Q. 13. Write the resonance structures for SO_3, NO_2 and NO_3^-.

Ans.



Q. 14. Use Lewis symbols to show electron transfer between the following atoms to form cations and anions : (*a*) K and S (*b*) Ca and O (*c*) Al and N.

Ans. *Refer Solved Example 4.(Page 7)*

Q. 15. Although both CO_2 and H_2O are triatomic molecules, the shape of H_2O molecule is bent while that of CO_2 is linear. Explain this on the basis of dipole moment.

Ans. CO_2 has zero dipole moment. This means that CO_2 molecule is linear so that the two C = O bond moments get cancelled giving zero resultant dipole moment. However, H_2O molecule has resultant dipole moment showing that it cannot be linear.The two O–H bonds are arranged in angular shape and the bond moment of two O–H bonds give resultant dipole moment.

Q. 16. Write the significance/applications of dipole moment.

Ans. *Refer Text (Page 24).*

Q. 17. Define electronegativity. How does it differ from electron gain enthalpy ?

Ans. *Refer unit 3.*

Q. 18. Explain with the help of suitable example polar covalent bond.

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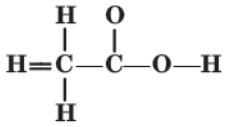
Ans. The bond formed between atoms having different electronegativities is called polar covalent bond. Greater the difference in the electronegativities of the atoms forming the bond, greater will be the polarity of the molecule. For example, the following bonds are polar covalent bonds :

$\delta+\ \delta-$	$\delta+\ \delta-$	$\delta+\ \delta-$	$\delta+\ \delta-$
H—Cl	H—F	Br—Cl	O—H

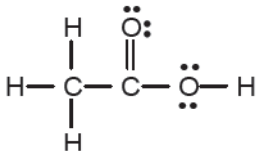
Q. 19. Arrange the bonds in order of increasing ionic character in the molecules: LiF, K_2O, N_2, SO_2 and ClF_3.

Ans. $N_2 < SO_2 < ClF_3 < K_2O < LiF$.

Q. 20. The skeletal structure of CH_3COOH as shown below is correct, but some of the bonds are shown incorrecctly. Write the correct Lewis structure for acetic acid.



Ans. Correct Lewis structure of CH_3COOH is



Q. 21. Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why CH_4 is not square planar ?

Ans. In square planar geometry, the bond angle will be 90° which is less than bond angle in tetrahedral geometry (109.5°). Therefore, repulsive forces between electron pairs will be more in square planar geometry and it will be less stable in comparison to tetrahedral geometry.

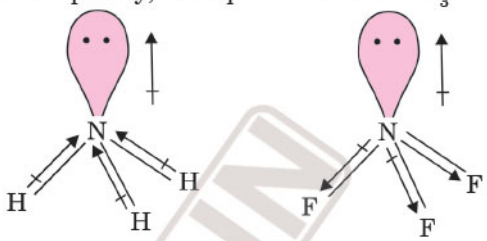
Q. 22. Explain why BeH_2 molecule has a zero dipole moment although, the Be—H bonds are polar.

Ans. BeH_2 molecule is linear molecule, therefore, the resultant dipole moment of two Be–H bonds get cancelled giving zero dipole moment.

$$H \rightleftharpoons Be \rightleftharpoons H \quad \mu = 0$$

Q. 23. Which out of NH_3 and NF_3 has higher dipole moment and why?

Ans. NH_3 has higher dipole moment than NF_3. Both NH_3 and NF_3 molecules have pyramidal shape with one lone pair on nitrogen atom. Fluorine is more electronegative that hydrogen and therefore, the N—F bonds should be more polar than N—H bonds. Consequently, the resultant dipole moment of NF_3 should be much larger than that of NH_3. However, the dipole moment of ammonia (μ = 1.47 D) is larger than that of NF_3 (μ = 0.24 D). This is due to the presence of lone pair on nitrogen. In case of NH_3, the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the three N—H bonds. Therefore, it adds on the resultant dipole moment of the N—H bonds. On the other hand, in case of NF_3, the orbital dipole is in the opposite direction to the resultant dipole moment of the three N—F bonds. Thus, the lone pair moments cancel the resultant N—F bond moments as shown in figure. Consequently, the dipole moment of NF_3 is low.



Q. 24. What is meant by hybridisation of atomic orbitals? Describe the shapes of *sp*, sp^2, sp^3 hybrid orbitals.

Ans. *Refer Text (Page 40-42).*

Q. 25. Describe the change in hybridisation (if any) of the Al atom in the following reaction :

$$AlCl_3 + Cl^- \longrightarrow AlCl_4^-$$

Ans. It changes from sp^2 (in $AlCl_3$) to sp^3 in $AlCl_4^-$.

Q. 26. Is there any change in the hybridisation of B and N atoms as a result of the following reaction ?

$$BF_3 + NH_3 \longrightarrow F_3B.NH_3$$

Ans. *Refer Solved Example 14. (Page 48)*

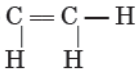
Q. 27. Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C_2H_4 and C_2H_2 molecules.

Ans. *Refer Text (Page 44–45).*

Q. 28. What is the total number of sigma and pi bonds in the following molecules ?

(*a*) C_2H_2 (*b*) C_2H_4

Ans. (*i*) H—C≡C—H — σ bonds = 3, π bonds = 2

(*ii*)  — σ bonds = 5, π bonds = 1

Q. 29. Considering x-axis as the internuclear axis which out of the following will not form a sigma bond and why ? (*a*) 1*s* and 1*s* (*b*) 1*s* and $2p_x$ (c) $2p_y$ and $2p_y$ (d) 1*s* and 2*s*.

Ans. Only (c) will not form a σ bond because taking x-axis as the internuclear axis, there will be sidewise overlap between the two $2p_y$ orbitals forming a π-bond. All others will form σ-bond.

Q. 30. Which hybrid orbitals are used by carbon atoms in the following molecules?

(*a*) $CH_3 — CH_3$ (*b*) $CH_3—CH=CH_2$
(*c*) $CH_3—CH_2—OH$ (*d*) $CH_3—CHO$
(*e*) CH_3COOH

Ans. *Refer Solved Example 13. (Page 48)*

Q. 31. What do you understand by bond pairs and lone pairs of electrons ? Illustrate by giving one example of each type.

Ans. *Refer Text (Page 27–28).*

Q. 32. Distinguish between a sigma and a pi bond.

Ans. *Refer Table 9, (Page 37).*

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Q. 33. Explain the formation of H_2 molecule on the basis of valence bond theory.

Ans. *Refer Text (Page 35-36).*

Q. 34. Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.

Ans. *Refer Text (Page 52).*

Q. 35. Use molecular orbital theory to explain why the Be_2 molecule does not exist.

Ans. M.O. electronic configuration of Be_2 molecule is

$Be_2 : K\,K\,(\sigma 2s)^2\,(\sigma^* 2s)^2$

Bond order = $\frac{2-2}{2} = 0$

Since bond order of Be_2 molecule is zero, therefore, Be_2 molecule does not exist.

Q. 36. Compare the relative stability of the following species and indicate their magnetic properties; O_2, O_2^+, O_2^- (superoxide) O_2^{2-} (peroxide)

Ans. *Refer Conceptual Questions [3], Q.6 (Page 69).*

Q. 37. Write the significance of a plus and a minus sign shown in representing the orbitals.

Ans. Plus and minus sign corresponds to sign of electron wave. The crests of a wave are usually given +ve sign and troughs of a wave are given –ve sign.

Q. 38. Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds?

Ans. *Refer Text (Page 29).*

Q. 39. Define hydrogen bond. Is it weaker or stronger than the van der Waals forces?

Ans. The attractive force which binds hydrogen atom of one molecule with electronegative atom (F, O or N) of another molecule is called hydrogen bond. Hydrogen bond is stronger than the van der Waals forces of attraction.

Q. 40. What is meant by the term bond order? Calculate the bond order of : N_2, O_2, O^+_2 and O^-_2.

Ans. Bond order is defined as the number of covalent bonds in a covalent molecule. It is equal to one half of the difference between the number of electrons in the bonding and antibonding molecular orbitals i.e.

$$\text{Bond order} = \frac{\text{No. of electrons in bonding M.Os.} - \text{No. of electrons in anti bonding M.Os.}}{2}$$

$N_2 : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\pi 2p_x)^2\;(\pi 2p_y)^2\,(\sigma 2p_z)^2$

$$\text{B.O} = \frac{8-2}{2} = 3$$

$O_2 : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2(\pi 2p_y)^2\,(\pi^* 2p_x)^1\,(\pi^* 2p_y)^1$

$$\text{B.O} = \frac{8-4}{2} = 2$$

$O_2^+ : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p_z)^2\;(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^* 2p_x)^1$

$$\text{B.O} = \frac{8-3}{2} = 2.5$$

$O_2^- : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p_z)^2\;(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^* 2p_x)^2\,(\pi^* 2p_y)^1$

$$\text{B.O} = \frac{8-5}{2} = 1.5$$

NCERT Exemplar Problems

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 104*

Short Answer Questions *Carrying 2 or 3 marks*

Q. 1. Explain the non-linear shape of H_2S and non-planar shape of PCl_3 using valence shell electron pair repulsion theory.

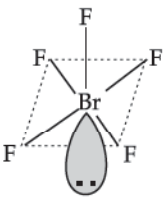
Ans. *Refer Text (Page 31; similar to H_2O and NH_3).*

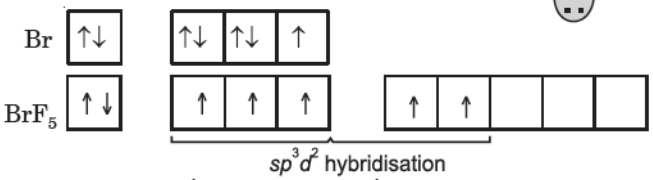
Q. 2. Using molecular orbital theory, compare the bond energy and magnetic character of O_2^+ and O_2^- species.

Ans. *Refer Text (Page 61-62).*

Q. 3. Explain the shape of BrF_5.

Ans. BrF_5 involves sp^3d^2 hybridisation and has one lone pair of electrons as :

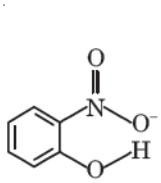




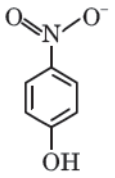
The shape is square pyramidal.

Subjective Questions

Q. 4. Structures of molecules of two compounds are given below :



(I)



(II)

(a) Which of the two compounds will have intermolecular hydrogen bonding and which compound is expected to show intramolecular hydrogen bonding ?

(b) Which of the above two compounds will show higher melting point?

(c) Which of the above compounds will form hydrogen bond with water easily and be more soluble in it ?

Ans. (a) Compound I will form intramolecular hydrogen bonding because NO_2 and OH groups are close together.

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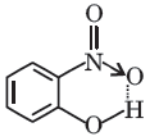
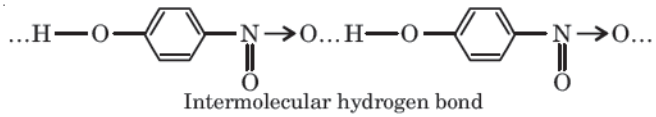
Compound II will form intermolecular hydrogen bonding.



I

Intramolecular hydrogen bond



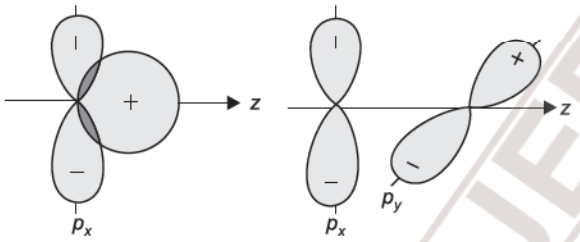
Intermolecular hydrogen bond

II

(*b*) Compound II will have higher melting point because during intermolecular hydrogen bond, more and more molecules are joined together through hydrogen bond formation.

(*c*) Because of intramolecular hydrogen bonding compound I will not be able to form hydrogen bonds with water. Therefore, compound I will be less soluble in water. On the other hand, compound II can form hydrogen bonds with water more easily and therefore, will be soluble in water.

Q. 5. Why does type of overlap given in the following figure not result in bond formation ?



Ans. In first figure, the ++ overlap is equal to + – overlap and therefore, these cancel out and net overlap is zero.

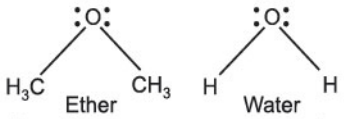
In second figure, no overlap is possible because the two orbitals are perpendicular to each other.

Q. 6. Explain why PCl_5 is trigonal bipyramidal whereas IF_5 is square pyramidal.

Ans. *Refer Text (Pages 29 and 33).*

Q. 7. In both water and dimethyl ether (CH_3—O—CH_3), oxygen atom is central atom, and has the same hybridisation, yet they have different bond angles. Which one has greater bond angle ? Give reason.

Ans. Dimethyl ether has larger bond angle than water. This is because there is more repulsion between bond pairs of CH_3 groups attached in ether than between bond pairs of hydrogen atoms attached to oxygen in water. The carbon of CH_3 group in ether is attached to three hydrogen atoms through σ bonds and electron pairs of these bonds add to the electron charge density on carbon atom. Hence, repulsion between two—CH_3 groups will be more than that between two H atoms.



Ether Water

Q. 8. Write Lewis structure of the following compounds and show formal charge on each atom.

HNO_3, NO_2, H_2SO_4.

Ans. *Refer Text (Pages 10-11).*

Q. 9. Write the complete sequence of energy levels in the increasing order of energy in the molecule. Compare the relative stability and the magnetic behaviour of the following species :

N_2, N_2^+, N_2^-, N_2^{2+}

Ans. *Refer Text (Page 61).*

Q. 10. What is the effect of the following processes on the bond order of N_2 and O_2 ?

(*a*) $N_2 \longrightarrow N_2^+ + e^-$

(*b*) $O_2 \longrightarrow O_2^+ + e^-$

Ans. (*a*) Bond order decreases from 3 to 2.5

(*b*) Bond order increases from 2 to 2.5

Q. 11. Give reasons for the following :

(*i*) Covalent bonds are directional bonds while ionic bonds are non-directional.

(*ii*) Water molecule has bent structure whereas carbon dioxide molecule is linear.

(*iii*) Ethyne molecule is linear.

Ans. *Refer Text.*

Q. 12. What is an ionic bond ? With two suitable examples explain the difference between an ionic and a covalent bond ?

Ans. *Refer Text.*

Q. 13. Arrange the following bonds in order of increasing ionic character giving reason.

N—H, F—H, C—H and O—H.

Ans. Electronegativity difference

N—H	F—H	C—H	O—H
3.0 – 2.1	4.0 – 2.1	2.5 – 2.1	3.5 – 2.1
= 0.9	= 1.19	= 0.4	= 1.4

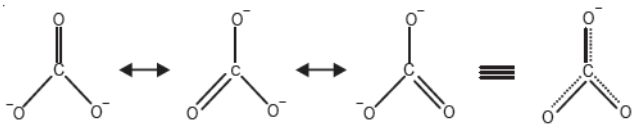
Increasing order of electronegativity difference :

C – H < N – H < O – H < F – H

Greater is the difference in electronegativity between two bonded atoms, greater is the ionic character.

Q. 14. Explain why CO_3^{2-} ion cannot be represented by a single Lewis structure. How can it be best represented ?

Ans. A single structure of carbonate cannot explain all the properties of the ions. It can be represented as resonance hybrid of the following structures :



According to a single structure, there are two types

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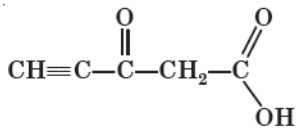
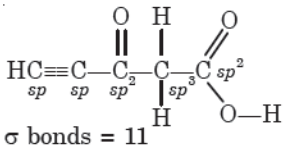
of bonds one double C = O and two single C – O bonds. But actually all the bonds are identical with same bond length and bond strength. This can be explained by resonance.

Q. 15. Predict the hybridisation of each carbon in the molecule of organic compound given below. Also indicate the total number of sigma and pi bonds in this molecule.



Ans.



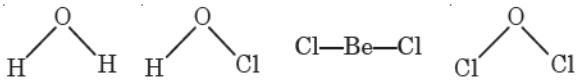
σ bonds = 11

π bonds = 4

Q. 16. Group the following as linear and non-linear molecules :

H_2O, HOCl, $BeCl_2$, Cl_2O.

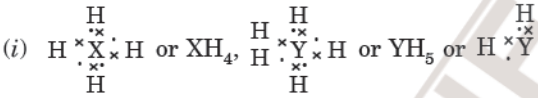
Ans.



Non–linear Linear Non–linear

Q. 17. Elements X, Y and Z have 4, 5 and 7 valence electrons respectively. (*i*) Write the molecular formula of the compounds formed by these elements individually with hydrogen. (*ii*) Which of these compounds will have the highest dipole moment ?

Ans. (*i*)



(*e.g.*, CH_4) (*e.g.*, PH_5)

or YH_3;

(*e.g.*, PH_3)

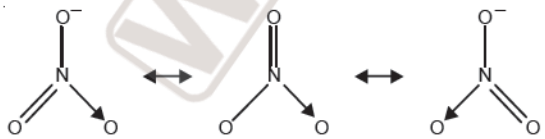
(*ii*) Z will be most electronegative element and hence HZ will have highest dipole moment.

Q. 18. Draw the resonating structure of

(*i*) Ozone molecule (*ii*) Nitrate ion.

Ans. (*i*)

(*ii*)



Q. 19. Predict the shapes of the following molecules on the basis of hybridisation.

BCl_3, CH_4, CO_2, NH_3.

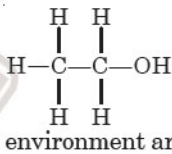
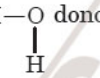
Ans. *Refer Text (Page 41–43).*

Q. 20. All the C—O bonds in carbonate ion (CO_3^{2-}) are equal in length. Explain.

Ans. On the basis of resonance. *Refer Text* and *NCERT Exemplar Problem Q. 14.*

Q. 21. What is meant by the term average bond enthalpy ? Why is there difference in bond enthalpy of O—H bond in ethanol (C_2H_5OH) and water ?

Ans. The average of the bond dissociation enthalpies of different bonds in polyatomic molecules (which contain more than one bond of the same type) is called average bond enthalpy.

The O—H bonds in ethanol,  and water  donot have similar environment around oxygen atom. Hence, their O—H bond enthalpies are different.

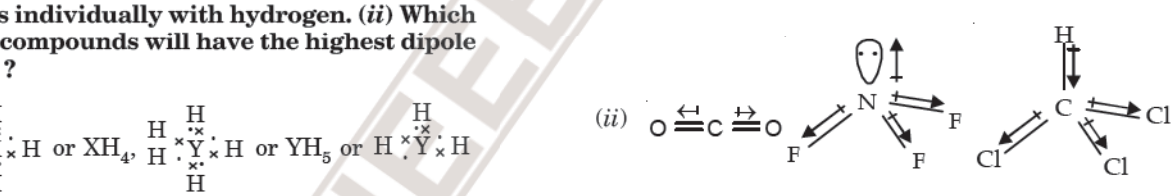
Long Answer Questions *Carrying 5 marks*

Q. 22. (*i*) Discuss the significance/applications of dipole moment.

(*ii*) Represent diagrammatically the bond moments and the resultant dipole moment in CO_2, NF_3 and $CHCl_3$.

Ans. (*i*) *Refer Text (Page 24).*

(*ii*)



μ = 0 μ = 0.24D μ = 1.02D

Q. 23. Use the molecular orbital energy level diagram to show that N_2 would be expected to have a triple bond, F_2, a single bond and Ne_2, no bond.

Ans. *Refer Text (Page 61).*

Q. 24. Briefly describe the valence bond theory of covalent bond formation by taking an example of hydrogen. How can you interpret energy changes taking place in the formation of dihydrogen ?

Ans. *Refer Text (Page 35).*

Q. 25. Describe hybridisation in the case of PCl_5 and SF_6. The axial bonds are longer as compared to equatorial bonds in PCl_5 whereas in SF_6 both axial bonds and equatorial bonds have the same bond length. Explain.

Ans. *Refer Text.*

Q. 26. (*i*) Discuss the concept of hybridisation. What are its different types in a carbon atom.

(*ii*) What is the type of hybridisation of carbon atoms marked with star

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(a) $\overset{*}{C}H_2 = CH - \overset{O}{\overset{\|}{\overset{*}{C}}} - O - H$

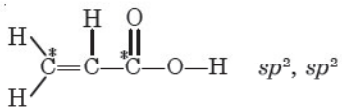
(b) $CH_3 - \overset{*}{C}H_2 - OH$

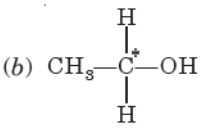
(c) $CH_3 - CH_2 - \overset{O}{\overset{\|}{\overset{*}{C}}} - H$

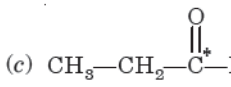
(d) $\overset{*}{C}H_3 - CH = CH - CH_3$

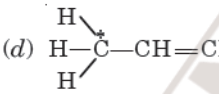
(e) $CH_3 - \overset{*}{C} \equiv CH$

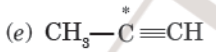
Ans. *(i) Refer Text (Page 36).*

(ii) (a)  sp^2, sp^2

(b)  sp^3

(c)  sp^2

(d)  sp^3

(e)  sp

QUICK MEMORY TEST

A. Say True or False

1. Ionic compounds are bad conductors of electricity in the solid state.
2. The shape of SF_6 molecule is octahedral whereas that of IF_7 is square pyramidal.
3. The bond order of CO molecule is 2.5.
4. As N—F bond is more polar than N—H bond, NF_3 molecule has higher dipole moment than NH_3.
5. The bond angle follows the order :

$$NH_4^+ > NH_3 > NH_2^-$$

6. The dipole moment of cis $C_2H_2Cl_2$ isomer is more than that of trans isomer.
7. N_2^+ has greater bond dissociation enthalpy than N_2 molecule.
8. Out of MgO and CaO, MgO is harder.
9. The *d*-orbital involved in dsp^2 hybridisation is $d_{x^2-y^2}$.
10. The dipole moment of CH_3F is greater than that of CH_3Cl.

B. Complete the missing links

1. During the change : $O_2 \longrightarrow O_2^+ + e^-$, bond order changes from ..... to .....
2. Ortho nitrophenol has ..... hydrogen bond while *p*-nitrophenol has ..... hydrogen bond.
3. In SF_4 molecule, S involves ..... hybridisation.
4. The *d*-orbitals involved in sp^3d^2 hybridisation are ..... and .....
5. The shape of ClF_3 molecule is .....
6. Out of H_2S, CO_2, BeF_2 and H_2O, the linear molecules are .....
7. The shape of BrF_5 molecule is .....
8. The number of lone pairs and bond pairs in XeF_4 molecule are ..... and .....
9. The bond order in O_2^+ species is .....
10. Out of HF, HCl, HBr and HI, the lowest boiling point is of ..... and highest boiling point is of .....

C. Choose the correct alternative

1. The bond in peroxide ion is *weaker/stronger* than in superoxide ion.
2. In N_2 molecule, energy of $\pi 2p_x$ and $\pi 2p_y$ MOs are *lower/higher* than $\sigma 2p_z$ MO.
3. The bond length of CO^+ is *more/less* than CO.
4. N_2 molecule is *paramagnetic/diamagnetic.*
5. The *d*-orbital involved in sp^3d hybridisation is $d_{z^2}/d_{x^2-y^2}$.
6. Bond angle of H_2O is *more/less* than that of H_2S.
7. The dipole moment of ortho dichlorobenzene is *more/less* than meta dichlorobenzene.
8. The bond length of sp^3(C—H) is *more/less* than sp^2(C—H) bond.
9. The shape of XeF_4 molecule is *tetrahedral/square planar.*
10. Dipole moment of NF_3 molecule is *more/less* than NH_3 molecule.
11. $[NiCl_4]^{2-}$ ion has *square planar/tetrahedral* geometry.
12. The bond angle of NO_2^+ is *more/less* than NO_2^-.
13. O_3 and NO_2^- are *isoelectronic/not isoelectronic.*
14. Bond order of O_2^+ is *1.5/2.5.*
15. Ice has *less/more* density than water.

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Answers QUICK MEMORY TEST

A. Say True or False

1. True
2. **False :** Shape of IF_7 is pentagonal bipyramidal.
3. **False :** Bond order of CO molecule is 3.
4. **False :** NF_3 has lower dipole moment than NH_3.
5. True
6. True
7. **True :** N_2 has bond order 3 and N_2^+ has bond order of 2.5.
8. **True :** Mg^{2+} ions are smaller than Ca^{2+} ions and therefore, lattice energy of MgO is larger and it is harder.
9. True
10. **False :** Though C—F bond is more polar than C—Cl bond due to greater electronegativity of F than Cl but C—F bond length is much smaller than C—Cl bond length.

B. Complete the missing links

1. 2, 2.5
2. intramolecular, intermolecular
3. sp^3d
4. $d_{x^2-y^2}$, d_{z^2}
5. T-shaped
6. BeF_2, CO_2
7. Square pyramidal
8. 2, 4
9. 2.5
10. HCl, HF.

C. Choose the correct alternative

1. weaker
2. lower
3. less
4. diamagnetic
5. d_{z^2}
6. more
7. more
8. more
9. square planar
10. less
11. square planar
12. more
13. isoelectronic
14. 2.5
15. less.

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. Which is expected to have the highest melting point :

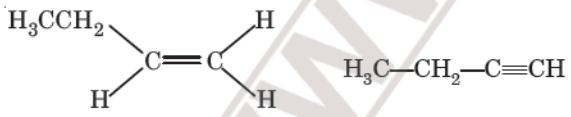
NH_3, $(CH_3)_3N$ or PH_3 ? Explain why ?

Ans. NH_3 has the strongest intermolecular forces (hydrogen bonding) and therefore, is expected to have the highest melting point.

Q.2. Which of the following has higher dipole moment and why ?

But-1-ene or But-1-yne

Solution: The structure of 1-butene and 1-butyne are:



But-1-ene

But-1-yne

In but-1-ene, each doubly bonded C-atom is sp^2 hybridised while in but-1-yne, each triply bonded C-atom is sp hybridised. Since sp-C is more electronegative than a sp^2C atom, therefore 1-butyne has higher dipole moment.

Q.3. Explain why melting point of NaCl is higher than that of $AlCl_3$.

Ans. Melting point of NaCl is higher than that of $AlCl_3$ because of strong electrostatic forces between oppositely charged ions. On the other hand, $AlCl_3$ is a covalent compound with lesser forces of attraction.

Q. 4. Silver halides have low solubilities in water as compared to alkali metal halides. Explain.

Ans. Silver halides are least soluble in water though their lattice energies are almost of the same order as that of highly soluble alkali metal halides. This can be explained on the basis of the outer electronic configuration of silver ion. The electronic configuration of Ag^+ is : $4d^{10}\ 5s^0\ 5p^0$. The electronic configuration of alkali metal ions, Li^+, Na^+ or K^+ is ns^0. We know that the d-electrons screen the nuclear charge from the outer electrons less effectively than s and p-electrons because of their poor penetration. Therefore, the effective nuclear charge, experienced by Ag^+ ion is much more than effective nuclear charge in alkali metal ions. Due to greater nuclear charge, the Ag^+ ion polarises the halide ion more strongly than alkali metal ion. Hence, it undergoes appreciable change from pure ionic character to covalent character. Because of the covalent character, the silver halides are less ionic and consequently their solubility in polar water is low.

Q.5. Which homonuclear diatomic molecule besides O_2 is paramagnetic ?

Ans. B_2 because its electronic configuration is:

$$B_2 : KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^1(\pi 2p_y)^1$$

Q.6. Distinguish between antibonding and nonbonding orbitals.

Ans. Antibonding orbitals have higher energies than the highest atomic orbital from which they are formed. On the other hand, nonbonding orbitals have the same energy as the atomic orbitals from which they are formed.

Q.7. Anhydrous $AlCl_3$ is covalent but $AlCl_3$. $6H_2O$ is ionic in nature. How would you account for this?

Ans. Anhydrous $AlCl_3$ is covalent while $AlCl_3$. $6H_2O$ is ionic in nature. The third ionisation energy of aluminium is

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very high. Therefore, a large amount of energy is needed to convert Al atom into Al^{3+} ion.

$$Al(g) + 5114 \text{ kJ mol}^{-1} \longrightarrow Al^{3+}(g) + 3e^-$$

Therefore, aluminium prefers to form covalent bonds with chlorine atoms forming covalent $AlCl_3$. However, when dissolved in water, it undergoes hydration liberating hydration energy.

$$AlCl_3 + 6H_2O \longrightarrow AlCl_3.\ 6H_2O + \text{Energy}$$
$$\text{Hydrated}$$

$$[Al(H_2O)_6]^{3+} + 3Cl^-$$

The hydration energy released provides energy for the removal of 3 electrons from aluminium atom. In fact, aluminium does not exist as simple aluminium ion (Al^{3+}) but in the form of a complex ion $[Al(H_2O)_6]^{3+}$. Thus, hydrated aluminium chloride is ionic in nature.

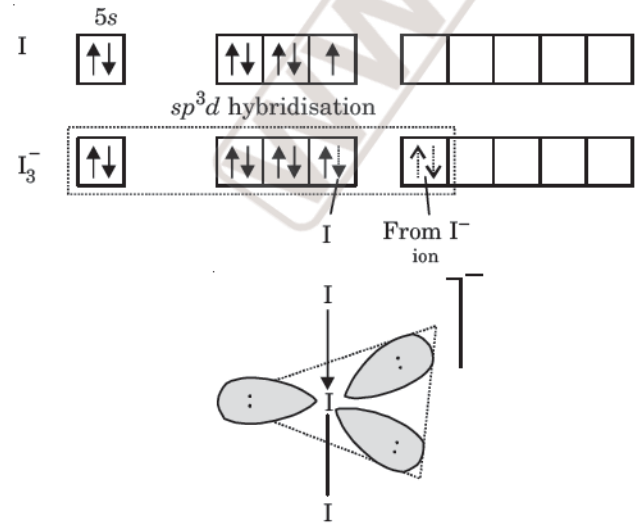
Q.8. Cu^+ and Na^+ are of same size but CuCl is insoluble while NaCl is soluble in water. Explain.

Ans. In NaCl, the hydration energy is sufficient to overcome the lattice energy of ionic NaCl. Hence NaCl is soluble in water. The high hydration energy of NaCl is because of relatively high ionic character of NaCl with the result that water dipoles interact strongly with Na^+ and Cl^- ions.

On the other hand, CuCl has sufficiently covalent character because of greater polarization of Cu^+ ion *(refer Q.4)* . As a result of covalent character, its hydration energy is low and is not sufficient to overcome the lattice energy of CuCl. Consequently, it is insoluble in water.

Q.9. Account for the linear shape of I_3^- ion.

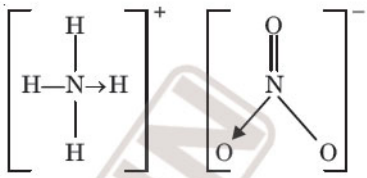
Ans. The central I atom has the ground state electronic configuration as $5s^2\ 5p^5$. It involves sp^3d hybridization involving one 5*s*, three 5*p* and one vacant 5*d* orbital. The half filled sp^3d hybrid orbital forms a covalent bond with one I atom and an empty sp^3d hybrid orbital accepts an electron pair from I^- ion to form a coordinate bond. Thus, the geometry of the molecule is trigonal bipyramidal in which three positions are occupied by lone pairs.



Because of the equivalent positions of lone pairs the resulting I_3^- ion is linear.

Q.10. Indicate the types of bonds present in NH_4NO_3 and state the mode of hybridisation of two N atoms.

Ans.



NH_4^+ ion contains three covalent bonds and one dative bond (formed by the donation of lone pair of electrons on N in NH_3 to H^+ ion).

NO_3^- ion contains covalent and dative bonds.

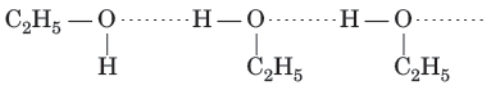
The bond between NH_4^+ and NO_3^- is ionic.

N of NH_4^+ ion is sp^3 hybridised and the shape of NH_4^+ ion is tetrahedral. N of NO_3^- ion is sp^2 hybridised and the shape of NO_3^- ion is planar.

Q.11. Which one has high boiling point and why ?

Ethyl alcohol or dimethyl ether.

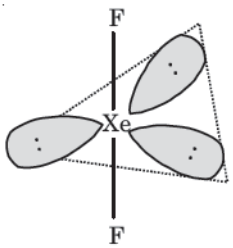
Ans. Ethyl alcohol (C_2H_5OH) has higher boiling point because of hydrogen bonding in its molecules.



There is no hydrogen bonding in dimethyl ether ($C_2H_5OC_2H_5$).

Q.12. XeF_2 molecule is linear molecule but it is sp^3d hybridized. Why ?

Ans. Due to sp^3d hybridisation, it has trigonal bipyramidal geometry in which three positions are occupied by lone pairs of electrons. The lone pairs are present in equatorial positions and their resultant effect is zero. As a result, the bonds are formed by axial Xe—F bonds only which are at an angle of 180° to each other.



Q.13. Name and represent the types of bonds present in $CuSO_4.5H_2O$.

Ans. $CuSO_4.5H_2O$ has ionic, covalent, coordinate and hydrogen bonds as shown ahead :

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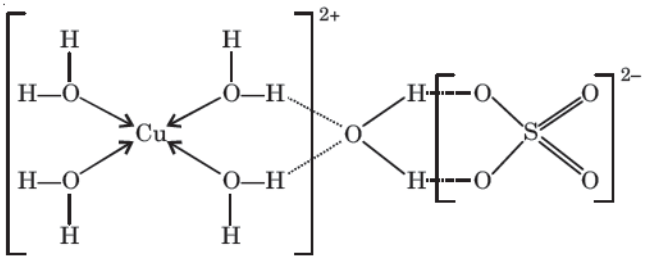
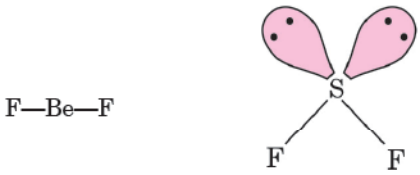


In $CuSO_4 . 5H_2O$, four H_2O molecules are bonded to Cu^{2+} ion by coordinate bonds whereas fifth H_2O molecule is linked by hydrogen bonds between two coordinated H_2O molecules and two oxygen atoms of sulphate ion.

Q.14. BeF_2 molecule is linear while SF_2 is angular though both are triatomic.

Ans. In BeF_2, Be is surrounded only by 2 electron bond pairs and therefore, the molecule is linear. On the other hand, in SF_2, the central atom S, is surrounded by 2 bond pairs and 2 lone pairs. Since it is surrounded by 4 electron pairs, the geometry is expected to be tetrahedral with two positions occupied by lone pairs.



2 bond pairs (Linear)

2 bond pairs, 2 lone pairs (Angular)

Because of the larger repulsions of lone pair-bond pair, the bond angle is less than 109.5° and the resultant molecule is angular.

Q.15. Is the bond order in superoxide ion more or less than in peroxide ion. Explain on the basis of MO theory.

Ans. The MO configuration of superoxide ion (O_2^-) is :

$$KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^1$$

$$\text{Bond order} = \frac{8-5}{2} = 1\frac{1}{2}$$

The MO configuration of peroxide ion is (O_2^{2-}) is

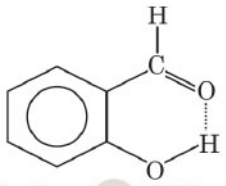
$$KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^2$$

$$\text{Bond order} = \frac{8-6}{2} = 1$$

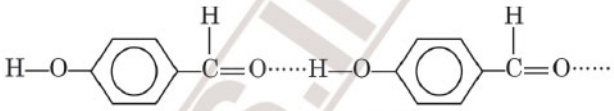
So, bond order in superoxide ion is more than in peroxide ion.

Q.16. Explain why o-hydroxybenzaldehyde is a liquid at room temperature while *p*-hydroxy-benzaldehyde is a high melting solid.

Ans. In o-hydroxybenzaldehyde, there is intramolecular hydrogen bonding which further prevents association of the molecules. However, in *p*-hydroxy benzaldehyde, there is intermolecular hydrogen bonding and therefore, there is association among the molecules :



o-hydroxybenzaldehyde
(intramolecular hydrogen bonding)



p-hydroxybenzaldehyde
(intermolecular hydrogen bonding)

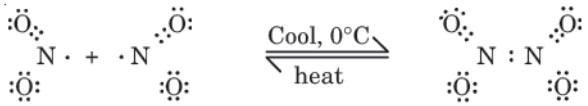
Thus, because of larger association, *p*-hydroxy benzaldehyde is a solid at room temperature but *o*-hydroxybenzaldehyde is a liquid because of less association.

Q.17. Nitrogen dioxide (NO_2) is paramagnetic at room temperature. When a sample of the gas is cooled below 0°C, its molecular weight increases and it loses its paramgnetism. When it is reheated, the behaviour is reversed.

***(i)* Using electron dot structure, write an equation which accounts for these observations.**

***(ii)* How does this phenomenon differ from resonance?**

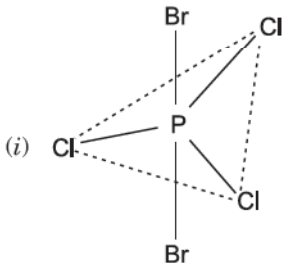
Ans. *(i)* NO_2 has one unpaired electron and is therefore, paramagnetic in nature. On cooling it forms dimer N_2O_4 which has higher molecular mass and is diamagnetic. This is represented as :



(ii) This is an equilibrium reaction and differs from resonance.

Q.18. Draw three possible geometrical structures of PBr_2Cl_3 and predict which of these have dipole moments.

Ans.



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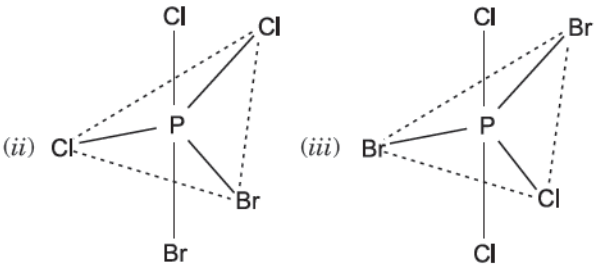
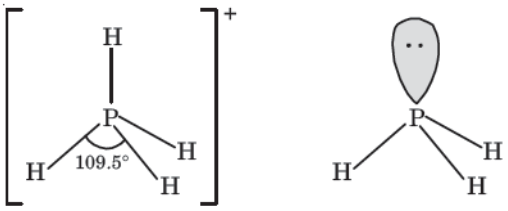


Structures (*ii*) and (*iii*) have dipole moments.

Q.19. Bond angle in PH_4^+ is higher than that in PH_3 why ?

Ans. Both PH_4^+ and PH_3 involve sp^3 hybridisation of P atom. In PH_4^+ all the four orbitals are bonded, whereas in PH_3 there is a lone pair of electrons on P. In PH_4^+, the HPH bond angle is tetrahedral angle of 109.5°. But in PH_3, lone pair-bond pair repulsion is more than bond pair-bond pair repulsion so that bond angles become less than normal tetrahedral angle 109.5°. The bond angle in PH_3 has been found to be about 93.6°.



Q.20. Why does PCl_5 exist as $[PCl_4]^+[PCl_6]^-$ in the crystalline state ?

Ans. PCl_5 has unsymmetrical structure because of different axial and equatorial bonds. Therefore, it is unstable and it changes to tetrahedral $[PCl_4]^+$ and octahedral $[PCl_6]^-$ ions, which have stable geometries.

Q.21. Explain the observations that the bond length in N_2^+ is 0.02Å larger than in N_2 while the bond length in NO^+ is 0.09Å less than in NO.

Ans. The electronic configurations are :

$$N_2 : KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2;\ \text{B.O.} \frac{8-2}{2} = 3$$

$$N_2^+ : KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^1;\ \text{B.O.} \frac{7-2}{2} = 2.5$$

$$NO : KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2 (\pi^* 2p_x)^1;\ \text{B.O.} \frac{8-3}{2} = 2.5$$

$$NO^+ : KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2;\ \text{B.O.} \frac{8-2}{2} = 3$$

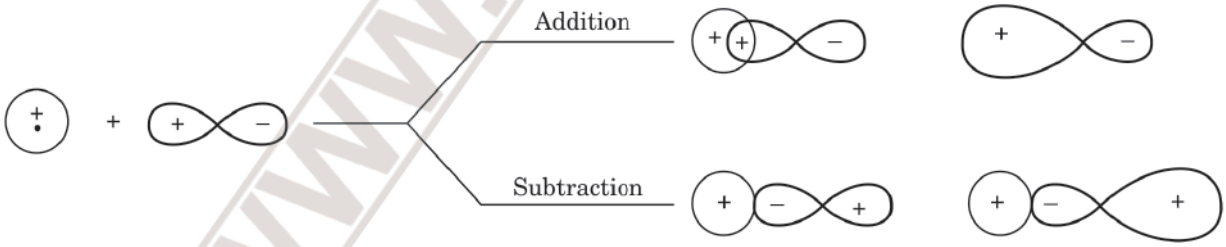
N_2 molecule has stronger bond than N_2^+ and therefore, N_2^+ has larger bond length than N_2. NO has weaker bond than NO^+ and therefore, NO^+ has smaller bond length than NO. Moreover, in comparison to ionization of N_2 which involves the loss of electron from bonding MO, the ionization of NO involves loss of electron from antibonding MO. Therefore, the decrease in bond length from NO to NO^+ is more than increase in bond length from N_2 to N_2^+.

Q.22. Which of the following combinations of orbitals are allowed in LCAO method (considering z-axis to be molecular axis) and sketch the shapes of MOs formed by their addition and subtraction :

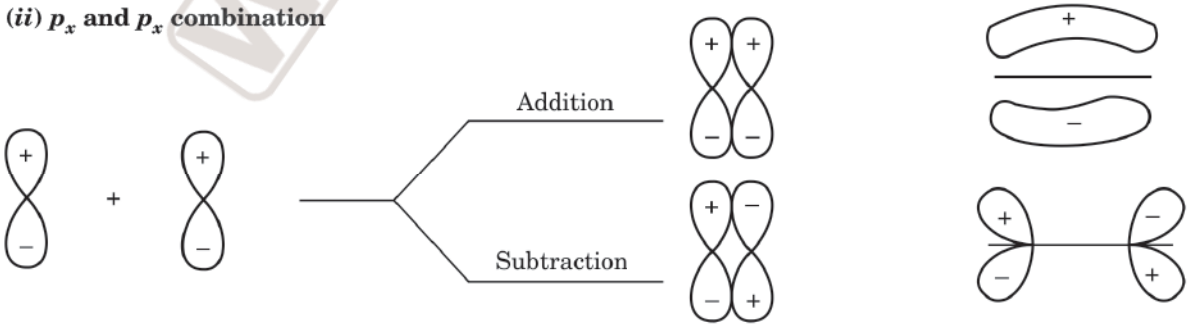
(*i*) *s* and p_z (*ii*) p_x and p_x (*iii*) p_z and p_y (*iv*) *s* and p_x

Ans. The allowed combinations are (*i*) *s* and p_z and (*ii*) p_x and p_x. Other combinations (*iii*) and (*iv*) are not allowed because they have zero overlap.

(*i*) *s* and p_z combination



(*ii*) p_x and p_x combination



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Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. Why are the noble gases monoatomic ?
2. Can a non-polar molecule have polar bonds ? Explain with an example.
3. Give one example each for a compound with (*a*) an ionic bond (*b*) a covalent bond.
4. Write Lewis dot structure for HCOOH.
5. Which hybrid orbitals are used by carbon atoms in $H_3C—CH = CH_2$
6. Write formal charges of the atoms in nitrite ion.
7. Which out of the two molecules OCS and CS_2 has a higher dipole moment and why ?
8. An element A has the electronic configuration $1s^2 2s^2 2p^6 3s^2$ and another element B has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^5$. What type of bond is formed between A and B ? Give its Lewis structure.
9. Define resonance.
10. How does the hybridisation of carbon atom in $CH_2 = CH_2$ change when it is hydrogenated to $CH_3 CH_3$?
11. Give two examples of molecules containing coordinate bond.
12. What are the shapes of (*i*) BF_3 and (*ii*) NH_3 molecules ?
13. Which of the two bonds : ionic or covalent is directional ?
14. Can a π-bond be formed without the formation of a σ-bond. How many σ-and π-bonds are formed in acetylene?
15. Draw Lewis structure of O^{2-} and N^{3-} ions.
16. Give bond angles in H_2O, CH_4 and SF_6 molecules.
17. Name the factors which favour the formation of an ionic bond.
18. Define dipole moment. What are its units ?
19. How many σ-and π-bonds are present in naphthalene ?
20. Out of MgO and NaCl, which has higher lattice energy ?
21. What is meant by bond pair of electrons and lone pair of electrons ?
22. Define electronegativity and dipole moment.
23. Give one example each of a tetraatomic molecule which is

    (*i*) Polar (*ii*) Non-polar.
24. Give one example each of a molecule having

    (*i*) 6 bond pairs

    (*ii*) 7 bond pairs around the central atom.
25. What is the total number of sigma bonds and pi bonds in

$$H_3C—\underset{\displaystyle H}{\underset{|}{C}}=\underset{\displaystyle H}{\underset{|}{C}}—C \equiv C—H$$

26. What shapes are associated with sp^3d and sp^3d^2 hybrid orbitals ?
27. How is paramagnetic character of a compound related to the number of unpaired electrons ?
28. Which out of H_2^- and H_2^+ is more stable and why ?
29. Which *d*– orbitals are involved in sp^3d^2 hybridisation in SF_6 ?
30. Write the molecular orbital configuration of a molecule having bond order of three.
31. Which out of O_2^+ and O_2^- is more stable ?
32. Arrange the following molecular species in order of increasing stability :

$$N_2,\ N_2^+,\ N_2^{2-},\ N_2^{2+}$$

33. What is the shape of SF_6 molecule ?
34. Give one example of a molecule involving sp^3d hybrdisation.
35. Although chlorine has the same electronegativity as nitrogen, it does not form hydrogen bonding. Explain.
36. Why does formic acid exist as dimer ?
37. Why does KHF_2 exist but $KHCl_2$ does not ?
38. State the type of hybrid orbitals associated with (*i*) P in PCl_5 and (*ii*) S in SF_6. *(D.S.B. 2001)*
39. Which one of two : O_2^- and O_2^{2-} has higher bond order and why ?
40. What is the effect of the following ionization processes on the bond order in C_2 and O_2 ?

    (*i*) $C_2 \longrightarrow C_2^+ + e^-$ (*ii*) $O_2 \longrightarrow O_2^+ + e^-$

    (A.I.S.B. 2002)
41. What is the effect on the interatomic bond length of the following ionization processes ?

    (*i*) $N_2 \longrightarrow N_2^+ + e^-$ (*ii*) $C_2 \longrightarrow C_2^+ + e^-$

    (A.I.S.B. 2002)
42. Which one of the following has highest bond order ?

    N_2, N_2^+ or N_2^- *(A.I.S.B. 2002)*
43. Draw a diagram showing the formation of bonding and anti-bonding molecular orbitals by LCAO in homonuclear hydrogen molecule. *(D.S.B. 2004)*
44. Which of the two : ice or water has lower density ?
45. Do N_2^+ and O_2^+ have same bond order ?
46. Define bond length.

Short Answer Questions *carrying 2 or 3 marks*

1. Explain the formation of a chemical bond.
2. Explain the formation of a covalent bond. State two factors which influence the formation of a covalent bond.

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3. Write the favourable factors for the formation of ionic bond ?

4. Define octet rule. Write its significance and limitations.

5. What do you understand by a chemical bond ? Why do atoms combine to form compounds ?

6. Draw Lewis symbols for the following elements :

B, Ge, Si, Ar, Ca, K, As, Br.

7. Give one example of a compound containing double bond and one containing a triple bond.

8. Explain that whereas H_2 and F_2 are non-polar, HF is polar.

9. Draw the orbital representation of the molecules :

HF, H_2O and NH_3.

10. Write the Lewis dot structures of (*i*) CCl_4 (*ii*) PH_3 and (*iii*) BCl_3. Is the octet rule is obeyed in these structures ?

11. Draw the shapes of the following hybrid orbitals :

sp, sp^2, sp^3

12. Considering Z-axis as the internuclear axis, which out of the following will form a sigma bond :

(*i*) 1*s* and 1*s* (*ii*) 1*s* and $2p_z$ (*iii*) $2p_x$ and $2p_x$

(*iv*) $2p_x$ and $2p_y$ (*v*) $2p_y$ and $2p_y$

13. Give the Lewis dot structures of NH_3, CH_4 and SO_3.

14. Draw electron dot structures of the following :

(*i*) OF_2 (*ii*) C_2H_2

(*iii*) PCl_3 (*iv*) H_2O_2.

15. What is octet rule ? List important exceptions to octet rule.

16. Give the number and types of various bonds in acetylene molecule. Name the type of overlap responsible for each bond.

17. Draw dipole moment diagrams showing polarity of individual bonds and resultant dipole of the following :

(*i*) H_2O (*ii*) CO_2

(*iii*) BeF_2 (*iv*) BF_3.

18. Describe a co-ordinate bond, giving one example. How does it differ from a covalent bond ?

19. Give a schematic representation of various attractive and repulsive forces when two hydrogen atoms approach each other to form a molecule of hydrogen.

20. The dipole moment of hydrogen halides decreases from HF to HI. Explain this trend.

21. Write the formal charges of the atoms in

(*i*) hydroxide ion (*ii*) carbonate ion

(*iii*) nitrite ion.

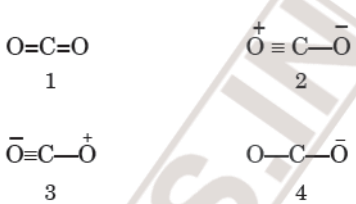
22. Sketch the bond moments and resultant dipole moments in the following molecules :

PCl_3, H_2O, NH_3, NF_3

23. Write resonance structures for SO_3, NO_2 and NO_3^-.

24. What is polar covalent bond ? Give two examples of compounds containing polar covalent bonds.

25. What is resonance ? What are the guidelines for writing resonating structures. Out of the following four resonance structures for the CO_2 molecule, which are important for describing the bonding in the molecules and why ?



1 2

3 4

26. Which of the two : KCl or Cl_2 has higher boiling point and why ?

27. Presence of lone pairs distorts the geometry of a molecule. Explain with example.

28. What do you understand by the term hybridisation ? Using the concept, explain the shapes of C_2H_4 and C_2H_2.

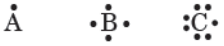
29. Define hybridisation. Discuss the bonding in acetylene molecule on the basis of hybridisation.

30. Write resonance structures for SO_3, NO_2 and NO_3^-.

31. Write the significance and applications of dipole moment.

32. Name the two bonds present in oxygen molecule and compare their strengths.

33. Three elements have the following Lewis symbols :



(*a*) Place the elements in the appropriate group of the periodic table.

(*b*) Which elements are most likely to form ions ? What is the expected charge on the ions ?

(*c*) Write the formulae and Lewis structures of the covalent compounds formed between:

(*i*) A and B (*ii*) A and C.

34. Explain the difference between sigma bond and pi-bond.

35. Define lattice enthalpy. How is it related to the stability of an ionic compound ?

36. What are the guidelines of writing resonating structures?

37. Explain sp^2 hybridisation and discuss the geometry of a molecule involving this type of hybridisation.

38. How do you account for equal bond lengths in ozone molecule ?

39. Define dipole moment. How does this help to predict the geometries of H_2O and CO_2 ?

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40. Draw diagrams showing the formation of double bond and a triple bond between carbon atoms in C_2H_4 and C_2H_2 molecules.

41. Explain the important aspects of resonance with reference to the CO_3^{2-} ion.

42. Explain with the help of suitable example, polar covalent bond.

43. In each of the following pairs, predict which has higher value of the property mentioned :

(*i*) HF, HCl : Polar character
(*ii*) NH_3, H_2O : Bond angle
(*iii*) KCl, KF : Lattice enthalpy
(*iv*) NF_3, NH_3 : Dipole moment
(*v*) C_2H_2, C_2H_4 : *s*-character in the hybridisation of carbon

44. Explain the term dipole moment. Name two molecules which have dipole moment and two molecules which do not have dipole moment. What is the significance of dipole moment ?

45. Using the concept of hybridisation, explain the shapes of BF_3, C_2H_4 and C_2H_2 molecules.

46. The electronic configurations of five neutral atoms are given below :

A : $1s^2\ 2s^2\ 2p^6\ 3s^2$;
B : $1s^2\ 2s^2\ 2p^6\ 3s^1$
C : $1s^2\ 2s^2\ 2p^1$;
D : $1s^2\ 2s^2\ 2p^3$
E : $1s^2\ 2s^2\ 2p^6$

Write the empirical formula for the substances containing:

(*i*) A and D (*ii*) B and D
(*iii*) D and D (*iv*) E and E.

47. Each carbon-oxygen bond in CO_2 molecule is polar and the molecule is non-polar. Explain.

48. Which out of NH_3 and NF_3 has higher dipole moment and why ?

49. Draw electron dot representation of :

(*i*) acetylene
(*ii*) ammonia.

50. What is dipole moment ? How does it affect the polarity of the molecule ? Which of the following molecules do you expect to be polar ?

CO, CCl_4, H_2O, BF_3, NH_3 and CO_2.

51. Explain the formation of H_2 molecule on the basis of valence bond theory.

52. Each carbon-oxygen bond in carbon dioxide molecule is polar but the molecule itself is non-polar. Explain.

53. CO_2 and H_2O both are triatomic molecules but there is large difference in their dipole moment values. Explain.

54. Explain the following :

(*a*) HCl is a covalent compound but it ionises in the solution.

(*b*) The molecule of $MgCl_2$ is linear whereas that of $SnCl_2$ is angular.

55. Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.

56. Why is it that in SF_4 molecule, the lone pair of electrons occupies an equatorial position in the overall trigonal bipyramidal arrangement in preference to an axial position ?

57. Explain the important aspects of resonance with reference to CO_3^{2-} ion.

58. Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds ?

59. Explain how does the valence bond theory account for

(*i*) a carbon–carbon double bond (C=C)

(*ii*) a carbon–carbon triple bond (C≡C)

60. What do you understand by a molecular orbital ? What is the maximum number of electrons that can occupy a molecular orbital?

61. What do you understand by bonding and antibonding molecular orbitals ? Calculate the bond order for O_2^+ and O_2.

62. Discuss the conditions necessary for the combination of atomic orbitals. Sketch and discuss the combination of *p*-atomic orbitals to form molecular orbitals.

63. Draw molecular orbital energy level diagram for nitrogen molecule.

64. Using MO diagram and occupancy of electrons in orbitals, arrange the following molecular species in increasing order of their stabilities :

(*i*) H_2 (*ii*) H_2^- (*iii*) H_2^+

65. Fill in the blanks :

(*i*) During the process : $O_2 + e^- \longrightarrow O_2^-$, the electron is added to the ..... MO.

(*ii*) The bond order in O_2^+ is ..... than in O_2.

(*iii*) In O_2 molecule there are ..... electrons in antibonding valence MOs.

66. Draw energy level diagrams to show that N_2 has triple bond, O_2 has double bond, F_2 has single bond and Ne_2 has no bond.

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67. Is it correct to say that bond order always increases when an electron is lost ?

68. Compare the relative stability of the following species and indicate their magnetic properties (diamagnetic or paramagnetic)

O_2, O_2^+, O_2^- (superoxide ion), O_2^{2-} (peroxide ion)

69. Arrange the following species in order of increasing stability :

Li_2, Li_2^+ and Li_2^-

Justify your choice with a molecular orbital diagram.

70. How does molecular orbital theory account for the following ?

(*a*) Bond order of N_2 is greater than N_2^+ but the bond order of O_2 is less than that of O_2^+.

(*b*) Be_2 does not exist.

71. Sketch the shapes of MOs obtained by the overlap of

(*i*) two *s*-orbitals

(*ii*) end on overlap of two *p*-orbitals

(*iii*) sidewise overlap of two *p*-orbitals.

72. What is hybridisation ? What type of hybridisations are possible in the following geometries ?

(*i*) Square planar

(*ii*) Trigonal bipyramidal

(*iii*) Octahedral.

73. On the basis of hybridisation, discuss the structures of

(*i*) PCl_5

(*ii*) IF_7

(*iii*) SF_6.

74. Calculate the bond order of O_2^- and O_2^{2-} and explain their magnetic character.

75. Explain the following :

(*i*) O_2^- is paramagnetic but O_2^{2-} is not.

(*ii*) N_2 has higher bond order than NO.

76. Compare the relative stability of the following species and comment on their magnetic (diamagnetic or paramagnetic) behaviour :

O_2^- and N_2^+

Long Answer Questions *carrying 5 marks*

1. Explain the formation of hydrogen molecule on the basis of electrostatic interactions giving potential energy diagram. Explain why He_2 is not possible.

2. Discuss the formation of covalent bond according to orbital concept. Draw orbital overlap diagram for each of the following molecules :

(*a*) HF (*b*) NH_3 (*c*) C_2H_4

(*d*) BF_3 (*e*) OF_2.

3. Identify the type of bonds you would expect in :

(*a*) water (*b*) silicon

(*c*) aluminium (*d*) diamond

(*e*) chlorine.

4. What do you understand by electronegativity ? How is it useful in predicting polarity of molecules ?

5. Discuss the shapes of the following molecules on the basis of VSEPR theory :

(*i*) CH_4

(*ii*) PF_5

(*iii*) NH_3

(*iv*) H_2O

(*v*) SF_6.

6. Write short notes on

(*i*) Resonance

(*ii*) Coordinate covalent bond

(*iii*) σ and π bonds.

7. What is lattice energy ? Discuss Born Haber cycle for the determination of lattice energy of sodium chloride crystal.

8. Discuss the shape of the following molecules on the basis of VSEPR model

(*i*) $BeCl_2$

(*ii*) BCl_3

(*iii*) $SiCl_4$

(*iv*) AsF_5

(*v*) H_2S

(*vi*) PH_3

9. What is dipole moment ? Discuss its important applications.

10. What is hybridisation ? Discuss different types of hybridisation undergone by carbon.

11. With the help of molecular orbital theory, show that N_2 molecule has triple bond, O_2 molecule has double bond while F_2 molecule has single bond. Compare their bond strengths.

12. (*a*) Distinguish between the following :

(*i*) Bonding and antibonding MOs.

(*ii*) Sigma and pi bonds.

(*b*) What is hybridisation ? Discuss the shapes of the following on the basis of concept of hybridisation:

(*i*) SF_6 (*ii*) PF_5 (*iii*) $[Ni(CN)_4]^{2-}$

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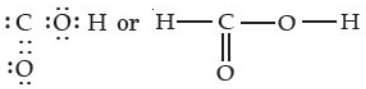
Hints & Answers for Revision Exercises

Very Short Answer Questions

2. Yes. Though the bonds in a molecule are polar, yet the arrangement of bonds is such that the overall polarity is zero. For example, CO_2 molecule has net zero dipole moment, but each CO bond is polar.

3. (*a*) Sodium chloride (*b*) Methane (CH_4)

4.  or

5. sp^3, sp^2, sp^2

7. OCS has higher dipole moment

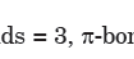
8. Ionic bond. $A^{2+}[B]^-_2$

10. From sp^2 ($CH_2 = CH_2$) to sp^3 ($CH_3 — CH_3$)

11. H_3O^+, O_3

12. (*i*) Trigonal planar (*ii*) Pyramidal

13. Covalent bond

14. No, σ-bonds = 3, π-bonds = 2 **15.** 

16. H_2O = 104.5°, CH_4 = 109.5°, SF_6 = 90°.

19. σ = 19, π = 5

20. MgO

23. (*i*) NH_3 (*ii*) BF_3

24. (*i*) SF_6 (*ii*) IF_7

25. σ = 10, π = 3

26. Trigonal bipyramidal, octahedral.

27. Larger the number of unpaired electrons, greater will be paramagnetic character

28. H_2^+ because it contains electrons only in bonding MOs.

29. $d_{x^2-y^2}$ and d_{z^2}

30. For N_2 : KK $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2$

31. O_2^+ because it has higher bond order (2.5) than O_2^- (1.5).

32. $N_2^{2-} < N_2^- < N_2^+ < N_2$

33. Octahedral

34. PF_5

35. The size of Cl is larger than N and therefore, it cannot form effective hydrogen bonding.

36. Due to hydrogen bonding.

37. Due to hydrogen bonding in HF as :

H—F.....H—F.....H—F.....

it can exist as HF_2^- ion and therefore forms KHF_2.

But there is no hydrogen bonding in HCl and it cannot form HCl_2^- ion.

39. (*i*) sp^3d (*ii*) sp^3d^2

40. (*i*) decreases (*ii*) increases

41. (*i*) increases (*ii*) decreases

42. N_2

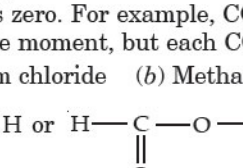
44. ice.

45. Yes, bond order in both N_2^+ and O_2^+ is 2.5.

Short Answer Questions Carrying 2 or 3 marks

6.

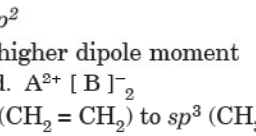
7. Double bond : O_2, Triple bond N_2.

10. (*i*) 

octet rule obeyed

(*ii*)

octet rule not obeyed

(*iii*) 

octet rule obeyed

12. (*i*) and (*ii*)

25. 1 and 2 are important.

26. KCl because it is ionic compound having strong electrostatic forces of attraction.

33. (*a*) A (group 1), B (group 14), C (group 17)

(*b*) The elements likely to form ions are A and C, charges A^+, C^-

(*c*)

43. (*i*) HF (*ii*) NH_3

(*iii*) KF (*iv*) NH_3

(*v*) C_2H_2

46. (*i*) A_3D_2 (*ii*) B_3D

(*iii*) $D_2(D \equiv D)$ (*iv*) E(mono atomic)

48. NH_3

50. CO, H_2O, NH_3

51. Water — Covalent, Ammonia — Covalent, Ethylene — Covalent, Sodium chloride — Ionic

65. (*i*) $\pi^* 2p_x$ (*ii*) more (*iii*) four

67. Bond order may increase or decrease when an electron is lost depending upon whether the electron is lost from bonding or antibonding MO.

72. (*i*) dsp^2 (*ii*) dsp^3 (*iii*) sp^3d^2

75. (*i*) O_2^- : KK$(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^1$

Paramagnetic due to the presence of 1 unpaired electron.

O_2^{2-} : KK$(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^2$

It is diamagnetic.

(*ii*) N_2 : KK $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi\, 2p_y)^2(\sigma\, 2p_z)^2$

$$\text{B.O.} = \frac{8-2}{2} = 3$$

NO : KK $(\sigma 2s)^2\,(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma^* 2p_z)^2\ (\pi^* 2p_x)^1$

$$\text{B.O.} = \frac{8-3}{2} = 2.5$$

$\therefore$ N_2 has higher bond order than NO.

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Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

❑ EFFECT OF ELECTRONEGATIVITY ON THE SHAPES OF MOLECULES

The electronegativities of the atoms present in the molecules have important effect on the shapes of the molecules.

(*i*) Effect of change of electronegativity of the central atom

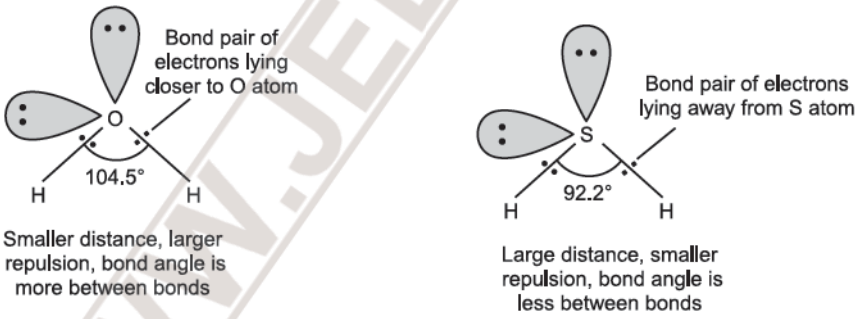
Consider the hydrides of Group VI elements. The hydrides H_2O, H_2S, H_2Se and H_2Te have four electron pairs (two bond pairs and two lone pairs) around the central atom. But their bond angles decrease in the order :

H_2O	H_2S	H_2Se	H_2Te
104.5°	92.6°	91°	90°

This may be easily explained in terms of electronegativities of the central atom as given below :

In the hydrides of Group VI elements, the central atom involves sp^3 hybridisation and is surrounded by four electron pairs; two lone pairs and two bond pairs. Due to the larger lone pair-lone pair repulsions, the bonded electron pairs are forced closer to each other and, therefore, the bond angle decreases from normal tetrahedral angle of 109.5°.

Now, as we move down the group from oxygen to tellurium, the size of the central atom goes on increasing and its electronegativity goes on decreasing. Consequently, the position of the bond pairs of electrons shifts more and more away from the central atom in moving from H_2O to H_2Te as shown in the figure. For example, as shown, the bond pair in O—H bond is closer to oxygen than the bond pair in S—H bond. As a result, the force of repulsion between the bonded pairs of electrons in H_2O is more than that in H_2S. In general, the force of repulsion between the bonded pairs of electrons decreases as we move from H_2O to H_2Te and, therefore, the bond angle also decreases in the same order.



Similar behaviour is observed in the case of hydrides of group V elements as given below :

NH_3	PH_3	AsH_3	SbH_3
107°	104°	92°	92°

(*ii*) Effect of change of electronegativity of the bonded atom

Take the example of halides of phosphorus (PX_3). The bond angles in these halides are observed as :

PF_3	PCl_3	PBr_3	PI_3
97°	100°	101.5°	100°

This can be explained on the basis of electronegativity of the atom attached to the central atom (*i.e.* halogen atom). In these molecules, P involves sp^3 hybridisation forming three sigma bonds and one position is occupied by a lone pair. The geometry may be described as pyramidal and as we move from PF_3 to PI_3, the electronegativity of the atom attached to the central phosphorus atom goes on decreasing. As a result, the bonding pair moves closer to the central

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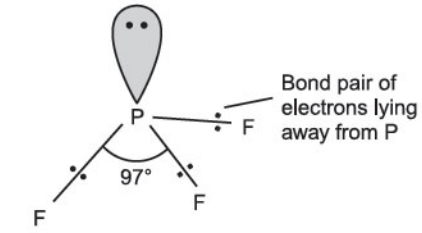
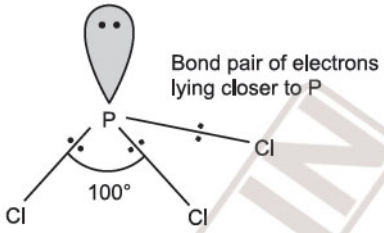
atom as shown. For example, as shown in figure, the bond pair in PF_3 is away from P (closer to F) than the bond pair in PCl_3. Therefore, the repulsive effect between the bonding pairs increases and hence bond angle increases.



Large distance, smaller repulsion, bond angle is less between bonds



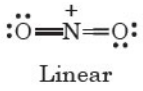
Smaller distance, larger repulsion, bond angle is greater between bonds

❑ EFFECT OF LONE PAIRS ON BOND ANGLE

The bond angle in NO_2, NO_2^+ and NO_2^- decreases as:

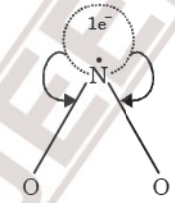
$$NO_2^+ > NO_2 > NO_2^-$$

The decreasing order of bond angle in NO_2^+, NO_2 and NO_2^- can be explained on the basis of presence of unshared electron and unshared electron pair. In NO_2^+, there is no unshared electron on N and therefore, the molecule is linear having bond angle of 180°. In NO_2, there is an unshared electron on N while in NO_2^-, there is an unshared electron pair on N-atom. The unshared electron pair causes more repulsion than an unshared electron. Therefore, the bond pairs in NO_2^- are forced more closer than in NO_2.

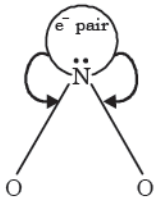


Linear

Bond angle = 180°



Bond angle = 132°



Bond angle = 115°

❑ CALCULATION OF TOTAL NUMBER OF BOND PAIRS AND LONE PAIRS AND PREDICTING SHAPES OF MOLECULES AND IONS

(*i*) Total no. of electron pairs around central atom

$= \frac{1}{2}$ (No. of valence electrons of the central atom + No. of atoms linked to central metal atom by single bonds).

For negative ions, **add** number of electrons equal to the units of negative charge on the ion to the number of valence electrons of the central atom and for positive ions **subtract** number of electrons equal to the units of positive charge from the valences electrons of the central atom.

(*ii*) No. of bond pairs (or shared pairs) = No. of atoms linked to central atom by single bonds.

(*iii*) No. of lone pairs = Total number of electron pairs – No. of bond pairs

Depending upon the number of electron pairs and the presence of lone pairs, shape can be predicted on the basis of Table 8 (Page 34).

Illustrations

ClF_3 : No. of valence electrons of the central Cl atom = 7

No. of electrons contributed by 3Cl atoms = 3

$\therefore$ Total no. of electron pairs around Cl atom $= \frac{7+3}{2} = 5$

No. of bond pairs = No. of atoms linked to Cl = 3

No. of lone pairs = 5 – 3 = 2

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Thus, molecule has trigonal bipyramidal shape with two positions occupied by lone pairs. Hence, its shape is **T-shaped.**

For quick solution, we can use the abbreviations as:
No. of valence electrons around central atom = Valence electrons;
No. of electrons contributed by atoms linked by single bonds = single bonds;
Total number of electron pairs = *ep*, No. of bond pairs = *bp*, No. of lone pairs = *ep*.

SF_4 : Valence electrons = 6, No. of single bonds = 4

$$e.p = \frac{6+4}{2} = 5,\ bp = 4,\ lp\ 5-4 = 1$$

Since it has 5 *ep*, the shape will be pentagonal bipyramidal with one position occupied by lone pair. Hence, its shape is **see-saw.**

BrF_5 : Valence electrons = 7, single bonds = 5

$$e.p = \frac{7+5}{2} = 6,\ bp = 5,\ lp = 6-5 = 1$$

Since it has 6 *ep*, its geometry will be octahedral with one position occupied by a lone pair. Hence, it has **square pyramidal shape.**

NH_4^+ : Valence electrons = 5, single bonds = 4, unit positive charge = 1

$$e.p = \frac{5+4-1}{2} = 4,\ bp = 4,\ lp = 4-4 = 0$$

It has **tetrahedral shape.**

NH_2^- : Valence electrons = 5, single bonds = 2, unit negative charge = 1

$$e.p = \frac{5+2+1}{2} = 4,\ bp = 2,\ lp = 4-2 = 2$$

It has tetrahedral geometry with two positions occupied by lone pairs. Its shape is **bent** or **v-shape.**

XeF_4: Valence electrons = 8, single bonds = 4

$$e.p = \frac{8+4}{2} = 6,\ bp = 4,\ lp = 6-4 = 2$$

Since it has 6 *ep*, its geometry will be octahedral with two positions occupied by lone pairs. Hence, it has square **planar shape.**

PREDICTING TYPE OF HYBRIDISATION OF CENTRAL ATOM IN A MOLECULE / ION AND SHAPES OF MOLECULES

The structure of a molecule can be predicted on the basis of hybridisation. The type of hybridisation can be known by the following **general formula.**

$$N = \frac{1}{2}\left[\begin{array}{l}\text{No. of electrons in}\\ \text{valence shell of}\\ \text{of central atom}\end{array} + \begin{array}{l}\text{No. of monovalent}\\ \text{atoms}\end{array} - \begin{array}{l}\text{Charge on}\\ \text{cation}\end{array} + \begin{array}{l}\text{Charge}\\ \text{on anion}\end{array}\right]$$

or $N = \frac{1}{2}$ [V + M – C + A], where N is the number of orbitals hybridised.

For example,

Value of N :	2	3	4	5	6	7
Hybridisation :	*sp*	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

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In some cases, the hybrid orbitals may be occupied by lone pair of electrons. Number of lone pairs of electrons may be calculated as :

L = N – M – D, where, D is number of divalent atoms.

Illustrations :

⇒ **Type I :** Central atom is surrounded by monovalent atoms only *e.g.* BeF_2, BCl_3, CH_4, PCl_5, PCl_3, H_2O, NH_3, $TeCl_4$, SCl_2, ClF_3, SF_4, XeF_2, XeF_4, SF_6, etc.

e.g. **PF_5**

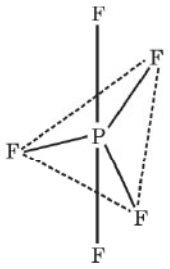
Here, V = 5, M = 5, C = 0, A = 0

$N = \frac{1}{2}[5 + 5 - 0 + 0] = 5$

***sp*³*d* hybridisation**

L = 5 – 5 = 0

No lone pair



Trigonal bipyramidal

ClF_3

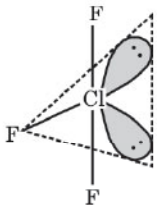
Here, V = 7, M = 3, C = 0, A = 0

$N = \frac{1}{2}[7 + 3 - 0 - 0] = 5$

***sp*³*d* hybridisation**

L = 5 – 3 – 0 = 2

It contains 2 lone pairs.



T-shaped

→ **Type II :** Central atom is surrounded by divalent atoms only *e.g.* SO_2, CO_2, CS_2, XeO_3, SO_3, etc.

e.g. **SO_3**

Here, V = 6, M = 0, C = 0, A = 0

$N = \frac{1}{2}[6 + 0 - 0 + 0] = 3$

***sp*² hybridisation**

L = 3 – 3 = 0

No lone pair.

Trigonal planar

XeO_3

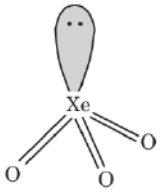
Here, V = 8, M = 2, C = 0, A = 0

$N = \frac{1}{2}[8 + 0 + 0 - 0] = 4$

***sp*³ hybridisation**

L = 4 – 3 = 1

It contains one lone pair.



Pyramidal

⇒ **Type III :** Central atom is surrounded by monovalent as well as divalent atoms *e.g.* $COCl_2$, $XeOF_2$, XeO_2F_2, $XeOF_4$, $POCl_3$ etc.

e.g. **$POCl_3$**

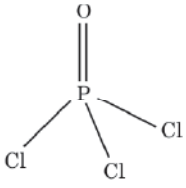
Here, V = 5, M = 3, C = 0, A = 0

$N = \frac{1}{2}[5 + 3 - 0 + 0] = 4$

***sp*³ hybridisation**

L = 4 – 3 – 1 = 0

No lone pair.



Tetrahedral

$XeOF_2$

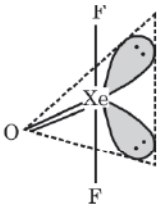
Here, V = 8, M = 2, C = 0, A = 0

$N = \frac{1}{2}[8 + 2 - 0 + 0] = 5$

***sp*³*d* hybridisation**

L = 5 – 2 – 1 = 2

Two lone pairs.



T-shaped

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⇒ **Type IV :** Hybridisation in cations *e.g.* NH_4^+, CH_3^+, H_3O^+, etc.

e.g. **NH_4^+**

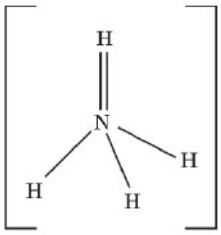
Here, V = 5, M = 4, C = 1, A = 0

$N = \frac{1}{2}[5 + 4 - 1 + 0] = 4$

***sp*³ hybridisation**

L = 4 – 4 = 0

No lone pair.



Tetrahedral

⇒ **Type V :** Hybridisation in anions *e.g.* CO_3^{2-}, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, ClO_3^-, ClO_4^-, etc.

e.g. **SO_4^2**

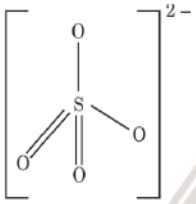
Here, V = 6, M = 0, C = 0, A = 2

$N = \frac{1}{2}[6 + 0 - 0 + 2] = 4$

***sp*³ hybridisation**

L = 4 – 0 – 4 = 0

No lone pair.



Tetrahedral

ClO_3^-

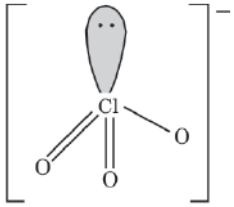
Here, V = 7, M = 0, C = 0, A = 1

$N = \frac{1}{2}[7 + 0 - 0 + 1] = 4$

***sp*³ hybridisation**

L = 4 – 0 – 3 = 1

One lone pair.



Pyramidal

⇒ **Type VI :** Hybridisation in complex ions e.g. I_3^-, ICl_2^-, ICl_4^-, ClF_2^-, etc.

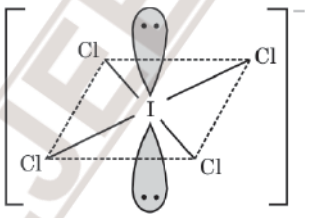
e.g. **ICl_4^-**

V = 7, M = 4, C = 0, A = 1

$N = \frac{1}{2}[7 + 4 - 0 + 1] = 6$

***sp*³*d*² hybridisation**

L = 6 – 4 – 0 = 2



Square planar

OBJECTIVE TYPE QUESTIONS

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Select the Correct Answers :

Chemical Bonds and Bond Polarity

A1. Which of the following molecules is not an exception to octet rule?
(*a*) BF_3 (*b*) PF_5 (*c*) CO_2 (*d*) IF_7.

A2. Which of the following has maximum covalent character?
(*a*) LiI (*b*) LiF (*c*) LiCl (*d*) LiBr.

A3. Which of the following has highest lattice energy
(*a*) LiF (*b*) NaF (*c*) KF (*d*) RbF.

A4. Which of the following molecule has net dipole moment ?
(*a*) CCl_4 (*b*) C_2H_2 (*c*) BF_3 (*d*) NH_3.

A5. The percentage ionic character of a bond having 1.275 Å its length and 1.03 D its dipole moment is :
(*a*) 10% (*b*) 15% (*c*) 16.83% (*d*) 18.8%.

A6. The correct order of dipole moment is
(*a*) $CH_4 < NF_3 < NH_3 < H_2O$
(*b*) $NF_3 < CH_4 < NH_3 < H_2O$
(*c*) $CH_4 < NH_3 < NF_3 < H_2O$
(*d*) $H_2O < NH_3 < NF_3 < CH_4$.

Answers

A1. (*c*) **A2.** (*a*) **A3.** (*a*) **A4.** (*d*) **A5.** (*c*) **A6.** (*a*)

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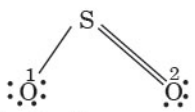
A7. Formal charge on two O atoms in



(a) –1, +1 (b) –1, 0
(c) 0, + 1 (d) –1, –1.

A8. Which of the following ion has maximum polarising power ?

(a) Na^+ (b) Mg^{2+}
(c) Ca^{2+} (d) Al^{3+}

A9. Which of the following is not correct resonating structure for carbon dioxide ?

(a) O = C = O (b) $^-O - C \equiv O^+$
(c) $^+O - C \equiv O^-$ (d) $^+O \equiv C - O^-$.

Shapes of Molecules

A10. The bond angles in molecules H_2O, NH_3, CH_4 and CO_2 are in the order :

(a) $H_2O > NH_3 > CH_4 > CO_2$
(b) $H_2O < NH_3 < CO_2 < CH_4$
(c) $H_2O < NH_3 < CH_4 < CO_2$
(d) $H_2O > NH_3 < CH_4 > CO_2$.

A11. The hybridisation of C involved in acetylene is :

(a) sp^2 (b) sp^3
(c) sp (d) dsp^2.

A12. For which of the following hybridisation the bond angle is maximum ?

(a) sp^2 (b) sp
(c) sp^3 (d) dsp^2.

A13. The angle between covalent bonds is maximum in

(a) CH_4 (b) BF_3
(c) PF_3 (d) NH_3.

A14. The percentage *s*-character of the hybrid orbitals in methane, ethene and ethyne are

(a) 25, 50, 75 (b) 25, 33, 75
(c) 25, 33, 50 (d) 100, 50, 25.

A15. CO_2 is isostructural with

(a) $SnCl_2$ (b) $ZnCl_2$
(c) $HgCl_2$ (d) C_2H_4.

A16. In an octahedral structure, the pair of *d*-orbitals involved in d^2sp^3 hybridisation is ?

(a) $d_{x^2-y^2}, d_{xz}$ (b) d_{z^2}, d_{zx}
(c) d_{xy}, d_{yz} (d) $d_{x^2-y^2}, d_{z^2}$

A17. Which of the following has highest bond angle ?

(a) NO_2^+ (b) NO_2
(c) NO_2 (d) NO_3.

A18. Which of the following molecules does not contain a lone pair of electrons ?

(a) NH_3 (b) PF_5
(c) H_2O (d) SF_4

A19. In which of the following molecules, the central atom has two lone pairs of electrons ?

(a) SF_4 (b) BrF_5
(c) SO_2 (d) XeF_4

A20. What typs of hybridisation is possible in square planar molecules ?

(a) sp^3d (b) dsp^3
(c) dsp^2 (d) sp^3d^2.

A21. PCl_5 molecule has the following geometry :

(a) Trigonal bipyramidal
(b) Octahedral
(c) Square plannar
(d) Plannar triangular.

A22. In which of the following molecules are all the bonds not equal ?

(a) BF_3 (b) AlF_3
(c) NF_3 (d) ClF_3

(C.B.S.E. Med 2006)

Molecular Orbital Theory

A23. Which of the following molecule/ion does not contain unpaired electrons ?

(a) N_2^+ (b) O_2^{2-}
(c) O_2 (d) B_2

A24. The calculated bond order in O_2^- ions is :

(a) 1 (b) 1½
(c) 2 (d) 2½

A25. If *z*–axis is considered as molecular axis, which of the following combinations is not possible for homonuclear diatomic molecules ?

(a) $2p_z + 2s$ (b) $2p_y - 2p_y$
(c) $2p_x + 2p_x$ (d) $2p_x + 2p_y$.

A26. Which of the following is paramagnetic ?

(a) O_2^- (b) CN^-
(c) CO (d) NO^+.

A27. Which one of the following pairs consists of only paramagnetic species ?

(a) O_2, NO (b) O_2^+, O_2^{2-}
(c) CO, NO (d) NO, NO^+

Answers

A7. (b) **A8.** (d) **A9.** (c) **A10.** (c) **A11.** (c) **A12.** (b) **A13.** (b) **A14.** (c) **A15.** (c) **A16.** (d)
A17. (a) **A18.** (b) **A19.** (d) **A20.** (c) **A21.** (a) **A22.** (d) **A23.** (b) **A24.** (b) **A25.** (d) **A26.** (a)
A27. (a)

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A28. The correct order of bond order values among the following is

(*i*) NO^- (*ii*) NO^+ (*iii*) NO (*iv*) NO^{2+} (*v*) NO^{2-}

(*a*) (*i*) < (*iv*) < (*iii*) < (*ii*) < (*v*)

(*b*) (*v*) = (*ii*) < (*i*) < (*iv*) < (*iii*)

(*c*) (*v*) < (*i*) < (*iv*) = (*iii*) < (*ii*)

(*d*) (*ii*) < (*iii*) < (*iv*) < (*i*) < (*v*)

A29. Which of the following is not paramagnetic ?

(*a*) O_2 (*b*) N_2^+

(*c*) B_2 (*d*) O_2^{2-}

A30. The bond strength is maximum in

(*a*) O_2^+ (*b*) O_2^-

(*c*) O_2 (*d*) O_2^{2-}

Hydrogen Bonding

A31. Hydrogen bond is strongest in

(*a*) S — H.....O (*b*) O — H.....S

(*c*) F — H.....F (*d*) F — H.....O

A32. The pair likely to form strongest hydrogen bonding is

(*a*) H_2O_2 and H_2O

(*b*) HCOOH amd CH_3COOH

(*c*) CH_3COOH and CH_3COOCH_3

(*d*) SiH_4 and $SiCl_4$

A33. Which of the following has highest boiling point?

(*a*) NH_3 (*b*) PH_3

(*c*) SbH_3 (*d*) AsH_3

A34. Which of the following has lowest boiling point?

(*a*) HF (*b*) HCl

(*c*) HI (*d*) HBr

A35. Which of the following statement is not true about water ?

(*a*) Water has more density than ice.

(*b*) Each water molecule is linked to four water molecules tetrahedrally

(*c*) In water, each O atom is bonded to 2-H atoms by hydrogen bonds.

(*d*) Water has minimum denisity at 277 K.

Answers

A28. (*c*) **A29.** (*d*) **A30.** (*a*) **A31.** (*c*) **A32.** (*b*) **A33.** (*a*) **A34.** (*b*) **A35.** (*d*)

B MULTIPLE CHOICE QUESTIONS *from Competitive Examinations*

AIPMT& Other State Boards' Medical Entrance

B1. The electronegativity difference between N and F is greater than that between N and H yet the dipole moment of NH_3 (1.5 D) is larger than that of NF_3 (0.2 D). This is because :

(*a*) in NH_3 the atomic dipole and bond dipole are in the same direction whereas in NF_3, these are in opposite directions.

(*b*) in NH_3 as well as NF_3 the atomic dipole and bond dipole are in opposite directions.

(*c*) in NH_3 the atomic dipole and bond dipole are in the opposite directions whereas in NF_3, these are in the same direction

(*d*) in NH_3 as well as in NF_3 the atomic dipole and bond dipole are in the same direction.

(C.B.S.E. Med 2006)

B2. Which of the following is not a correct statement ?

(*a*) The canonical structures have no real existence.

(*b*) Every AB_5 molecule does in fact have square pyramid structure.

(*c*) Multiple bonds are always shorter than corresponding single bonds.

(*d*) The electron-deficient molecules can act as Lewis acids. *(C.B.S.E. Med 2006)*

B3. In which of the following pairs, the two species are isostructural :

(*a*) BrO_3^- and XeO_3

(*b*) SF_4 and XeF_4

(*c*) SO_3^{2-} and NO_3^-

(*d*) BF_3 and NF_3 *(C.B.S.E. Med. 2007)*

B4. The correct order of C—O bonds length among CO, CO_3^{2-}, and CO_2 is

(*a*) $CO < CO_2 < CO_3^{2-}$

(*b*) $CO_2 < CO_3^{2-} < CO$

(*c*) $CO < CO_3^{2-} < CO_2$

(*d*) $CO_3^{2-} < CO_2 < CO$. *(C.B.S.E.Med. 2007)*

B5. According to molecular orbital theory, which of the lists ranks the nitrogen species in terms of increasing bond order ?

(*a*) $N_2^{2-} < N_2^- < N_2$

(*b*) $N_2 < N_2^{2-} < N_2^-$

(*c*) $N_2^- < N_2^{2-} < N_2$

(*d*) $N_2^- < N_2 < N_2^{2-}$ *(C.B.S.E. PMT 2009)*

B6. In which of the following molecules/ions BF_3, NO_2^-, NH_2^- and H_2O, the central atom is sp^2 hybridised ?

(*a*) NH_2^- and H_2O (*b*) NO_2^- and H_2O

(*c*) BF_3 and NO_2^- (*d*) NO_2^- and NH_2^-

(C.B.S.E. PMT 2009)

Answers

B1. (*a*) **B2.** (*b*) **B3.** (*a*) **B4.** (*a*) **B5.** (*a*) **B6.** (*c*)

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B7. In which one of the following species the central atom has the type of hybridization which is not the same as that present in the other three ?
(a) $SbCl_5^{2-}$ (b) PCl_5
(c) SF_4 (d) I_3^- *(C.B.S.E. Med. 2010)*

B8. Which one of the following species does not exist under normal conditions ?
(a) B_2 (b) Li_2
(c) Be_2^+ (d) Be_2 *(C.B.S.E. Med. 2010)*

B9. Among the following molecules : SO_2, SF_4, ClF_3, BrF_5 and XeF_4 which of the following shapes does not describe any of the molecules mentioned ?
(a) Bent (b) Trigonal bipyramidal
(c) See-saw (d) T-shape
(e) Square pyramidal *(Kerala PMT 2011)*

B10. Which of the following has the minimum bond length?
(a) O_2^+ (b) O_2^-
(c) O_2^{2-} (d) O_2 *(A.I.P.M.T. 2011)*

B11. Which of the two ions from the list given below have the geometry that is explained by the same hybridization of orbitals : NO_2^-, NO_3^-, NH_2^-, NH_4^+, SCN^- ?
(a) NO_2^- and NO_3^- (b) NH_4^+ and NO_3^-
(c) SCN^- and NH_2^- (d) NO_2^- and NH_2^-
(A.I.P.M.T. 2011)

B12. The pair of species with the same bond order is
(a) O_2^{2-}, B_2 (b) O_2^+, NO^+
(c) NO, CO (d) N_2, O_2 *(A.I.P.M.T. 2012)*

B13. Which of the following species contains three bond pairs and one lone pair around the central atom?
(a) H_2O (b) BF_3
(c) NH_2^- (d) PCl_3 *(A.I.P.M.T. 2012)*

B14. Which one of the following pairs is isostructural (*i.e.*, having the same shape and hybridization)?
(a) [BCl_3 and $BrCl_3$]
(b) [NH_3 and NO_3]
(c) [NF_3 and BF_3]
(d) [BF_4^- and NH_4^+] *(A.I.P.M.T. 2012)*

B15. Bond order of 1.5 is shown by
(a) O_2^+ (b) O_2^-
(c) O_2^{2-} (d) O_2 *(A.I.P.M.T. 2012)*

B16. Which of the following is a polar molecule ?
(a) SiF_4 (b) XeF_4
(c) BF_3 (d) SF_4
(NEET 2013)

B17. Which of the following is paramagnetic ?
(a) CN^- (b) NO^+
(c) CO (d) O_2^- *(NEET 2013)*

B18. Which one of the following molecules contains no π bond ?
(a) SO_2 (b) NO_2
(c) CO_2 (d) H_2O *(NEET 2013)*

B19. The bond orders for O_2^+ and C_2 respectively are
(a) 2.5, 2 (b) 3, 2
(c) 2, 2.5 (d) 2, 3
(e) 3, 3 *(Kerala PMT 2014)*

B20. Which of the following molecules has the maximum dipole moment ?
(a) CO_2 (b) CH_4
(c) NH_3 (d) NF_3 *(AIPMT 2014)*

B21. Which one of the following species has plane triangular shape ?
(a) N_3 (b) NO_3^-
(c) NO_2^- (d) CO_2 *(AIPMT 2014)*

B22. Which of the following sets of molecules contain the same number of lone pairs of electrons in the central atom?
(a) SO_2, ClF_3, BrF_3 (b) SF_4, NH_3, O_3
(c) ClF_3, XeF_2, H_2O (d) H_2O, SF_4, NH_3
(e) NH_3, XeF_2, O_3 *(Kerala PMT 2015)*

B23. Which one of the following does not match with respect to the shape of the molecule?
(a) NH_3 – Trigonal pyramidal
(b) SF_4 – Tetrahedral
(c) H_2S – Bent
(d) XeF_4 – Square planar *(AIPMT 2015)*

B24. Find the pair that has the same bond order with dimagnetic and paramagnetic properties respectively.
(a) F_2 and O_2 (b) N_2 and O_2^{2-}
(c) Li_2 and B_2 (d) B_2 and O_2
(e) He and Ne *(Kerala PMT 2015)*

B25. Decreasing order of stability of O_2, O_2^-, O_2^+ and O_2^{2-}
(a) $O_2 > O_2^+ > O_2^{2-} > O_2^-$
(b) $O_2^- > O_2^{2-} > O_2^+ > O_2$
(c) $O_2^+ > O_2 > O_2^- > O_2^{2-}$
(d) $O_2^{2-} > O_2^- > O_2 > O_2^+$ *(AIPMT 2015)*

B26. In which of the following pairs, both the species are not isostructural?
(a) NH_3, PH_3 (b) XeF_4, XeO_4
(c) $SiCl_4$, PCl_4^+ (d) diamond, silicon carbide
(AIPMT 2015)

Answers

B7.	(a)	**B8.**	(d)	**B9.**	(b)	**B10.**	(a)	**B11.**	(a)	**B12.**	(a)	**B13.**	(d)	**B14.**	(d)	**B15.**	(b)	**B16.**	(d)
B17.	(d)	**B18.**	(d)	**B19.**	(a)	**B20.**	(c)	**B21.**	(b)	**B22.**	(b)	**B23.**	(b)	**B24.**	(c)	**B25.**	(c)	**B26.**	(b)

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B27. Which of the following pairs of ions are isoelectronic and isostructural?

(a) SO_3^{2-}, NO_3^- (b) ClO_3^-, SO_3^{2-}

(c) CO_3^{2-}, SO_3^{2-} (d) ClO_3^-, CO_3^{2-}

(AIPMT 2015, 2016)

B28. The correct bond order in the following species is

(a) $O_2^+ < O_2^- < O_2^{2+}$ (b) $O_2^- < O_2^+ < O_2^{2+}$

(c) $O_2^{2+} < O_2^+ < O_2^-$ (d) $O_2^{2+} < O_2^- < O_2^+$

(AIPMT 2015)

B29. Maximum bond angle at nitrogen is present in which of the following?

(a) NO_2^+ (b) NO_3^-

(c) NO_2 (d) NO_2^- *(AIPMT 2015)*

B30. Consider the molecules CH_4, NH_3 and H_2O. Which of the given statement is false?

(a) The H—O—H bond angle in H_2O is smaller than the H—N—H bond angle in NH_3.

(b) The H—C—H bond angle in CH_4 is larger than the H—N—H bond angle in NH_3.

(c) The H—C—H bond angle in CH_4, the H—N—H bond angle in NH_3, and the H—O—H bond angle in H_2O are all greater than 90°.

(d) The H—O—H bond angle in H_2O is larger than the H—C—H bond angle in CH_4. *(NEET 2016)*

B31. Predict the correct order among the following:

(a) bond pair – bond pair > lone pair – bond pair > lone pair – lone pair

(b) lone pair – bond pair > bond pair – bond pair > lone pair – lone pair

(c) lone pair – lone pair > lone pair – bond pair > bond pair – bond pair

(d) lone pair – lone pair > bond pair – bond pair > lone pair – bond pair *(NEET 2016)*

B32. Which one of the following compound shows the presence of intramolecular hydrogen bond?

(a) H_2O_2 (b) HCN

(c) Cellulose (d) Concentrated acetic acid *(NEET 2016)*

B33. The correct geometry and hybridization for XeF_4 are

(a) octahedral, sp^3d^2

(b) trigonal bipyramidal, sp^3d

(c) planar triangle, sp^3d^3

(d) square planar, sp^3d^2. *(NEET 2016)*

B34. The hybridizations of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are

(a) sp, sp^3 and sp^2 (b) sp^2, sp^3 and sp^3

(c) sp, sp^2 and sp^3 (d) sp^2, sp and sp^3

(AIEEE 2011, NEET 2016)

B35. Which of the following pair of compounds is isoelectronic and isostructural?

(a) Tel_2, XeF_2 (b) IBr_2^-, XeF_2

(c) IF_3, XeF_2 (d) $BeCl_2$, XeF_2 *(NEET 2017)*

B36. The species, having bond angles of 120° is

(a) ClF_3 (b) NCl_3

(c) BCl_3 (d) PH_3 *(NEET 2017)*

B37. Which one of the following pair of species have the same bond order ?

(a) O_2, NO^+ (b) CN^-, CO

(c) N_2, O_2^- (d) CO, NO *(NEET 2017)*

B38. Among CaH_2, BeH_2, BaH_2, the order of ionic character is

(a) $BeH_2 < CaH_2 < BaH_2$

(b) $CaH_2 < BeH_2 < BaH_2$

(c) $BeH_2 < BaH_2 < CaH_2$

(d) $BaH_2 < BeH_2 < CaH_2$ *(NEET 2018)*

B39. Consider the following species: CN^+, CN^-, NO and CN. Which one of these will have the highest bond order ?

(a) NO (b) CN^-

(c) CN^+ (d) CN *(NEET 2018)*

B40. In the structure of ClF_3, the number of lone pairs of electrons on central 'Cl' atom is

(a) one (b) two

(c) four (d) three *(NEET 2018)*

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B41. Which of the following molecules/ions do not contain unpaired electrons ?

(a) B_2 (b) N_2^+

(c) O_2 (d) O_2^{2-} *(A.I.E.E.E. 2006)*

B42. Which of the following hydrogen bonds is the strongest ?

(a) F—H.....F (b) O—H.....O

(c) O—H.....F (d) O—H.....N

(A.I.E.E.E. 2007)

B43. Which of the following pairs of species have the same bond order ?

(a) NO^+ and CN^+ (b) CN^- and NO^+

(c) CN^- and CN^+ (d) O_2^- and CN^-

(A.I.E.E.E. 2008)

Answers

B27. (b) **B28.** (b) **B29.** (a) **B30.** (d) **B31.** (c) **B32.** (c) **B33.** (d) **B34.** (c) **B35.** (b) **B36.** (c)
B37. (b) **B38.** (a) **B39.** (b) **B40.** (b) **B41.** (d) **B42.** (a) **B43.** (b)

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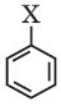
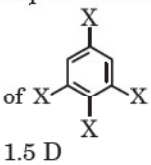
B44. The types of hybridisation on the five carbon atoms from left to right in the molecule

$CH_3—CH=C=CH—CH_3$ are

(a) $sp^3, sp^2, sp^2, sp^2, sp^3$
(b) $sp^3, sp, sp^2, sp^2, sp^3$
(c) $sp^3, sp^2, sp, sp^2, sp^3$
(d) $sp^3, sp^2, sp^2, sp, sp^3$
(e) sp^3, sp, sp, sp^2, sp^3 *(Kerala P.E.T. 2009)*

B45. Dipole moment of  is 1.5 D. The dipole moment of  is (X = halogen)

(a) 1.5 D (b) 2.25 D
(c) 1 D (d) 3 D *(West Bengal JEE 2010)*

B46. How many hydrogen bonded water molecule(s) are associated with $CuSO_4.5H_2O$?

(a) 1 (b) 2
(c) 3 (d) 4 *(AMU Engg. 2010, 2014)*

B47. Which one of the following conversions involve change in both hybridization and shape ?

(a) $CH_4 \rightarrow C_2H_6$ (b) $NH_3 \rightarrow NH_4^+$
(c) $BF_3 \rightarrow BF_4^-$ (d) $H_2O \rightarrow H_3O^+$ *(Karnataka CET 2010)*

B48. N_2 and O_2 are converted to monopositive cations N_2^+ and O_2^+ respectively. Which is incorrect ?

(a) In N_2^+ the N — N bond is weakened
(b) In O_2^+, the bond order increases
(c) In O_2^+, paramagnetism decreases
(d) N_2^+ becomes diamagnetic
(e) Both O_2 and O_2^+ are paramagnetic *(Kerala PET 2010)*

B49. The structure of IF_7 is

(a) square pyramid (b) trigonal bipyramid
(c) octahedral (d) pentagonal bipyramid *(A.I.E.E.E. 2011)*

B50. Likely bond angles of SF_4 molecule are

(a) 89°, 117° (b) 120°, 180°
(c) 45°, 118° (d) 117°, 92° *(A.I.E.E.E. 2011)*

B51. Which of the following has maximum number of lone pairs associated with Xe ?

(a) XeF_4 (b) XeF_6
(c) XeF_2 (d) XeO_3 *(A.I.E.E.E. 2011)*

B52. The number of types of bonds between two carbon atoms in calcium carbide is

(a) one sigma, one *pi*
(b) two sigma, one *pi*
(c) two sigma, two *pi*
(d) one sigma, two *pi* *(A.I.E.E.E. 2011)*

B53. The state of hybridization of the central atom and the number of lone pairs over the central atom in $POCl_3$ are

(a) *sp*,0 (b) sp^2, 0
(c) sp^3, 0 (d) dsp^2, 1 *(W.B.J.E.E. 2012)*

B54. The paramagnetic behaviour of B_2 is due to the presence of

(a) 2 unpaired electrons in π_b MO
(b) 2 unpaired electrons in π^* MO
(c) 2 unpaired electrons in σ^* MO
(d) 2 unpaired electrons in σ_b MO *(W.B.J.E.E. 2012)*

B55. Which one of the following contains ionic, covalent and co-ordinate bonds?

(a) NaOH (b) NaCl
(c) NaCN (d) NaNC *(Karnataka C.E.T. 2012)*

B56. In which of the following pairs the two species are not isostructural?

(a) PCl_4^+ and $SiCl_4$ (b) PF_5 and BrF_5
(c) AlF_6^{3-} and SF_6 (d) CO_3^{2-} and NO_3^- *(A.I.E.E.E. 2012)*

B57. The increasing order of O–N–O bond angle in the species NO_2, NO_2^+ and NO_2^- is

(a) $NO_2^+ < NO_2 < NO_2^-$
(b) $NO_2^- < NO_2 < NO_2^+$
(c) $NO_2^+ < NO_2^- < NO_2$
(d) $NO_2 < NO_2^+ < NO_2^-$ *(C.B.S.E. PMT. 2008, W.B. JEE 2013)*

B58. Molecular shapes of SF_4, CF_4 and XeF_4 and the number of lone pairs on the central atom are respectively.

(a) the same, with 1, 2 and 1
(b) the same, with 1, 0 and 1
(c) different, with 0, 1 and 2
(d) different, with 1, 0 and 2
(e) same, with 0, 0 and 1 *(Kerala P.E.T. 2013)*

B59. Allyl cyanide molecule contains

(a) 9 sigma bonds, 4 pi bonds and no lone pair
(b) 9 sigma bonds, 3 pi bonds and one lone pair
(c) 8 sigma bonds, 5 pi bonds and one lone pair
(d) 8 sigma bonds, 3 pi bonds and two lone pairs
(e) 6 sigma bonds, 2 pi bonds and four lone pairs *(Kerala P.E.T. 2013)*

Answers

B44. (c) **B45.** (a) **B46.** (a) **B47.** (c) **B48.** (d) **B49.** (d) **B50.** (a) **B51.** (c) **B52.** (d) **B53.** (c)
B54. (a) **B55.** (d) **B56.** (b) **B57.** (b) **B58.** (d) **B59.** (b)

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B60. In which of the following pairs of molecules/ions, both the species are not likely to exist ?
(a) H_2^-, He_2^{2+} (b) H_2^+, He_2^{2-}
(c) H_2^-, He_2^{2-} (d) H_2^{2+}, He_2
(JEE Main 2013)

B61. Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of
(a) $Li_2^- < Li_2 < Li_2^+$
(b) $Li_2 < Li_2^+ < Li_2^-$
(c) $Li_2^- < Li_2^+ < Li_2$
(d) $Li_2 < Li_2^- < Li_2^+$ *(JEE Main 2013)*

B62. The structure of XeF_6 is experimentally determined to be distorted octahedron. Its structure according to VSEPR theory is
(a) octahedron
(b) trigonal bipyramid
(c) pentagonal bipyramid
(d) tetragonal bipyramid. *(W.B. JEE 2014)*

B63. The bond angle in NF_3 (102.3°) is smaller than NH_3 (107.2°). This is because of
(a) large size of F compared to H
(b) large size of N compared to F
(c) opposite polarity of N in the two molecules
(d) small size of H compared to N. *(WB JEE 2014)*

B64. The lattice energy of NaCl is 788 kJ mol^{-1}. This means that 788 kJ of energy is required
(a) to separate one mole of solid NaCl into one mole of $Na^+(g)$ and one mole of $Cl^-(g)$ to infinite distance
(b) to separate one mole of solid NaCl into one mole of $Na(g)$ and one mole of $Cl(g)$ to infinite distance
(c) to convert one mole of solid NaCl into one mole of gaseous NaCl
(d) to convert one mole of gaseous NaCl into one mole of solid NaCl
(e) to separate one mole of gaseous NaCl into one mole $Na^+(g)$ and one mole of $Cl^-(g)$ to infinite distance.
(Kerala PET 2014)

B65. Molecular formulae and shapes of some molecules are given below. Choose the incorrect match.

Formula	— Shape
(a) NH_3	— Trigonal pyramidal
(b) SF_4	— Tetrahedral
(c) ClF_3	— T-shaped
(d) PCl_5	— Trigonal bipyramidal
(e) BF_3	— Trigonal planar

(Kerala PET 2014)

B66. The pair of compounds having identical shapes for their molecules is
(a) CH_4, SF_4 (b) BCl_3, ClF_3
(c) XeF_2, $ZnCl_2$ (d) SO_2, CO_2
(Karnataka CET 2014)

B67. The correct arrangement of species in the decreasing order of the bond length between carbon and oxygen in them is
(a) CO, CO_2, HCO_2^-, CO_3^{2-}
(b) CO_2, HCO_2^-, CO, CO_3^{2-}
(c) CO_3^{2-}, HCO_2^-, CO_2, CO
(d) CO, CO_3^{2-}, CO_2, HCO_2^- *(Karnataka CET 2014)*

B68. Which one of the following properties is not shown by NO?
(a) Its bond order is 2.5.
(b) It is diamagnetic in gaseous state.
(c) It is a neutral oxide.
(d) It combines with oxygen to form nitrogen dioxide.
(JEE Main 2014)

B69. The number of lone pairs of electrons on the central atoms of H_2O, $SnCl_2$, PCl_3 and XeF_2 respectively, are
(a) 2, 1, 1, ,3 (b) 2, 2, 1, 3
(c) 3, 1, 1, 2 (d) 2, 1, 2, 3 *(WB JEE 2015)*

B70. The correct order of O—O bond length in O_2, H_2O_2 and O_3 is
(a) $O_2 > O_3 > H_2O_2$ (b) $H_2O_2 > O_3 > O_2$
(c) $O_3 > O_2 > H_2O_2$ (d) $O_3 > H_2O_2 > O_2$
(WB JEE 2016)

B71. Identify the T-shaped molecule in the following:
(a) BF_3 (b) NH_3
(c) NF_3 (d) ClF_3
(e) PCl_3 *(Kerala PET 2016)*

B72. Which one of the following molecule has the least dipole moment?
(a) H_2O (b) BeF_2
(c) NH_3 (d) NF_3
(e) PF_3 *(Kerala PET 2016)*

B73. Main axis of diatomic molecule is z-axis. The orbitals p_x and p_y overlap to form
(a) π-molecular orbital
(b) σ-molecular orbital
(c) δ-molecular orbital
(d) no bond is formed *(Karnataka CET 2016)*

B74. The increasing order of bond orders of O_2, O_2^+, O_2^- and O_2^{2-} is
(a) O_2^+, O_2, O_2^-, O_2^{2-} (b) O_2^{2-}, O_2^-, O_2^+, O_2
(c) O_2, O_2^+, O_2^-, O_2^{2-} (d) O_2^{2-}, O_2^-, O_2, O_2^+
(Karnataka CET 2016)

B75. The species in which the N atom in a state of *sp* hybridisation is
(a) NO_2^+ (b) NO_2^-
(c) NO_3^- (d) NO_2 *(JEE Main 2016)*

B76. The ground state magnetic property of B_2 and C_2 molecules will be
(a) B_2 paramagnetic and C_2 diamagnetic
(b) B_2 diamagnetic and C_2 paramagnetic
(c) both are diamagnetic
(d) both are paramagnetic. *(WB JEE 2017)*

Answers

B60. (d) **B61.** (c) **B62.** (c) **B63.** (c) **B64.** (a) **B65.** (b) **B66.** (c) **B67.** (c) **B68.** (b) **B69.** (a)
B70. (b) **B71.** (d) **B72.** (b) **B73.** (d) **B74.** (d) **B75.** (a) **B76.** (a)

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B77. Which of the following structures of a molecule is expected to have three bond pairs and one lone pair of electrons?
(a) Trigonal Planar (b) Tetrahedral
(c) Octahedral (d) Pyramidal
(Karnataka CET 2017)

B78. Which of the following is the correct electron dot structure of N_2O molecule?
(a) :N≡N—Ö: (b) :N—N=Ö:
(c) :N=N=Ö: (d) :N≡N—Ö:⁻
(Karnataka CET 2017)

B79. Among the following, the molecule that will have the highest dipole moment is
(a) H_2 (b) HI
(c) HBr (d) HCl
(e) HF *(Kerala PET 2017)*

B80. Which of the following pairs have identical bond order?
(a) CN^- and NO^+ (b) CN^- and O_2^-
(c) CN^- and CN^+ (d) NO^+ and O_2^-
(e) O_2^- and CN^+ *(Kerala PET 2017)*

B81. Which of the following species is not paramagnetic?
(a) NO (b) CO
(c) O_2 (d) B_2 *(JEE Main 2017)*

B82. What will be the geometry of the compound MB_4L_2? Here B is bond pair and L is lone pair.
(a) Square planar (b) Octahedral
(c) Square pyramid (d) Tetrahedral
(J.K. CET 2018)

B83. What is the hybridisation and geometry of the given species? The species are XeF_2 and ICl_2^-
(a) sp^3d and trigonal bipyramidal
(b) sp^3d^2 and square planar
(c) sp^3d and linear
(d) sp^3 and irregular tetrahedron *(J.K. CET 2018)*

B84. Which of the following has the strongest H-bond?
(a) O – H --- S (b) S – H --- O
(c) F – H --- F (d) F – H --- O
(W.B. JEE 2018)

B85. The intramolecular hydrogen bond is present in
(a) phenol (b) *o*-nitrophenol
(c) *p*-nitrophenol (d) *p*-cresol
(Karnataka CET 2018)

B86. The state of hybrid orbitals of carbon in CO_2, CH_4 and CO_3^{2-} respectively is
(a) sp^3, sp^2 and sp (b) sp^3, sp and sp^2
(c) sp, sp^3 and sp^2 (d) sp^2, sp^3 and sp.
(Karnataka CET 2018)

B87. According to molecular orbital theory, which of the following will not be a viable molecule ?
(a) He_2^{2+} (b) He^{2+}
(c) H_2^- (d) H_2^{2-} *(JEE Main 2018)*

B88. Which of the following compounds contain(s) no covalent bond(s)?
KCl, PH_3, O_2, B_2H_6, H_2SO_4
(a) KCl, B_2H_6, PH_3 (b) KCl, H_2SO_4
(c) KCl (d) KCl, B_2H_6
(JEE Main 2018)

B89. Total number of lone pair of electrons in I_3^- ion is:
(a) 3 (b) 6
(c) 9 (d) 12 *(JEE Main 2018)*

B90. According to molecular orbital theory, which of the following is true with respect to Li_2^+ and Li_2^- ?
(a) Both are unstable
(b) Li_2^+ is unstable and Li_2^- is stable
(c) Li_2^+ is stable and Li_2^- is unstable
(d) Both are stable *(JEE Main 2019)*

B91. In which of the following processes, the bond order has increased and paramagnetic character has changed to diamagnetic ?
(a) $N_2 \longrightarrow N_2^+$ (b) $NO \longrightarrow NO^+$
(c) $O_2 \longrightarrow O_2^{2-}$ (d) $O_2 \longrightarrow O_2^+$ *(JEE Main 2019)*

B92. Total pi and half sigma bonds are present in
(a) N_2^+ (b) N_2
(c) O_2^+ (d) O_2 *(JEE Main 2019)*

JEE (Advance) for IIT Entrance

B93. The hybridisation of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ are
(a) sp, sp^3 and sp^2 respectively
(b) sp, sp^2 and sp^3 respectively
(c) sp^2, sp and sp^3 respectively
(d) sp^2, sp^3 and sp respectively.
(I.I.T. Screening 2000)

B94. Molecular shapes of SF_4, CF_4, and XeF_4 are
(a) the same with 2, 0 and 1 lone pairs of electrons respectively
(b) the same with 1, 1 and 1 lone pairs of electrons respectively
(c) different with 0, 1 and 2 lone pairs of electrons respectively
(d) different with 1, 0 and 2 lone pairs of electrons respectively. *(I.I.T. Screening 2000, AIEEE 2005, Kerala P.E.T. 2013)*

Answers

B77. (d) **B78.** (d) **B79.** (e) **B80.** (a) **B81.** (b) **B82.** (a) **B83.** (c) **B84.** (c) **B85.** (b) **B86.** (c)
B87. (d) **B88.** (c) **B89.** (c) **B90.** (d) **B91.** (b) **B92.** (a) **B93.** (b) **B94.** (d)

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B95. The correct order of hybridisation of the central atom in the following species : NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is

(*a*) dsp^2, dsp^3, sp^2 and sp^3

(*b*) sp^3, dsp^2, dsp^3, sp^2

(*c*) dsp^3, sp^2, sp^3, dsp^3

(*d*) dsp^2, sp^3, sp^2, dsp^3. *(I.I.T. Screening 2001)*

B96. Which of the following are isoelectronic and isostructural ?

NO_3^-, CO_3^{2-}, ClO_3^-, SO_3

(*a*) NO_3^-, CO_3^{2-}, (*b*) SO_3, NO_3^-,

(*c*) ClO_3^-, CO_3^{2-} (*d*) CO_3^{2-}, SO_3 *(I.I.T. 2003)*

B97. Total number of lone pair of electrons in $XeOF_4$ is ?

(*a*) 0 (*b*) 1

(*c*) 2 (d) 3 *(I.I.T. 2004)*

B98. Which species has the maximum number of lone pair of electrons on the central atom ?

(*a*) ClO_3^- (*b*) XeF_4

(*c*) SF_4 (*d*) $[I_3]^-$

(I.I.T. Screening 2005)

B99. The correct order of stability of the following resonance structures is

(I) $H_2C{=}N^+{=}N^-$

(II) $H_2C^+{-}N{=}N^-$

(III) $H_2C^-{-}N^+{\equiv}N$

(IV) $H_2C^-{-}N{=}N^+$

(*a*) I > II > IV > III (*b*) I > III > II > IV

(*c*) II > I > III > IV (*d*) III > I > IV > II

(I.I.T. JEE 2009)

B100. Assuming Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is

(*a*) 1 and diamagnetic

(*b*) 0 and diamagnetic

(*c*) 1 and paramagnetic

(*d*) 0 and paramagnetic *(I.I.T. 2010)*

B101. The species having pyramidal shape is :

(*a*) SO_3 (*b*) BrF_3

(*c*) SiO_3^{2-} (*d*) OSF_2 *(I.I.T. 2010)*

B102. The shape of XeO_2F_2 molecule is

(*a*) trigonal bipyramidal

(*b*) square planar

(*c*) tetrahedral

(*d*) see-saw *(I.I.T. J.E.E. 2012)*

Answers

B95. (*b*) **B96.** (*a*) **B97.** (*b*) **B98.** (*d*) **B99.** (*b*) **B100.** (*c*) **B101.** (*d*) **B102.** (*d*)

C MULTIPLE CHOICE QUESTIONS
with more than one correct answers

C1. Paramagnetic species are

(*a*) O_2^- (*b*) N_2

(*c*) C_2 (*d*) F_2

C2. The linear structure is possessed by

(*a*) $SnCl_2$ (*b*) CS_2

(*c*) NO_2^+ (*d*) SF_2

C3. Diamagnetic species are

(*a*) N_2 (*b*) O_2

(*c*) B_2 (*d*) O_2^{2-}

C4. Which of the following statements are not correct ?

(*a*) Hybrid orbitals form stronger bonds than *p*-orbitals.

(*b*) Promotion is essential for hybridisation.

(*c*) Boiling point of H_2O is more than H_2S.

(*d*) Resonance plays an important role in molecular orbital theory.

C5. In which of the following pairs, the shapes of the two molecules/ions is same ?

(*a*) H_2O, SF_2 (*b*) NH_3, SO_2

(*c*) PF_5, $SbCl_5$ (*d*) XeF_4, SF_4

C6. In which of the following pairs, both the molecules/ ions involve same type of hybridisation for the central atom ?

(*a*) SF_6, XeF_6 (*b*) NH_3, H_2O

(*c*) ClF_3, PF_5 (*d*) IF_7, $XeOF_4$

C7. In which of the following, the geometry is not correctly given ?

(*a*) PH_3 : Trigonal pyramidal

(*b*) SiH_4 : Tetrahedral

(*c*) ClF_3 : Trigonal planar

(*d*) SF_4 : Square planar

C8. CO_2 is isostructural with

(*a*) $SnCl_2$ (*b*) SF_2

(*c*) $HgCl_2$ (*d*) C_2H_2

Answers

C1. (*a,c*) **C2.** (*b,c*) **C3.** (*a,d*) **C4.** (*b,d*) **C5.** (*a,c*) **C6.** (*b,c*) **C7.** (*c,d*) **C8.** (*c,d*)

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C9. Hydrogen bonding plays a central role in the following phenomena :
(*a*) Ice floats in water.
(*b*) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions.
(*c*) Formic acid is more acidic than acetic acid.
(*d*) Dimerisation of acetic acid in benzene.
(*JEE Advance 2014*)

C10. The compound(s) with two lone pairs of electrons on the central atom is (are)
(*a*) BrF_5 (*b*) ClF_3
(*c*) XeF_4 (*d*) SF_4 (*JEE Advance 2016*)

C11. According to molecular orbital theory,
(*a*) C_2^{2-} is expected to be diamagnetic
(*b*) O_2^{2+} is expected to have a longer bond length than O_2
(*c*) N_2^+ and N_2^- have the same bond order
(*d*) He_2^+ has the same energy as two isolated He atom. (*JEE Advance 2016*)

C12. Which statements are correct for the peroxide ion?
(*a*) It has five completely filled anti-bonding molecular orbitals.
(*b*) It is diamagnetic.
(*c*) It has bond order one.
(*d*) It is isoelectronic with neon. (*W.B. JEE 2018*)

Answers

C9. (*a,b,d*) **C10.** (*b,c*) **C11.** (*a,c*) **C12.** (*b,c*)

D MULTIPLE CHOICE QUESTIONS
based on the given passage/comprehension

Passage I

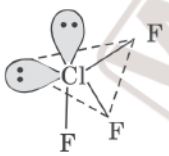
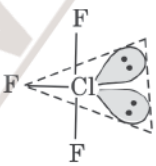
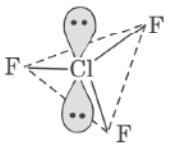
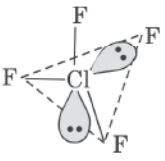
In order to explain the characteristic geometrical shapes of polyatomic molecules, Pauling introduced the concept of hybridisation. The orbitals undergoing hybridisation should have nearly same energy. There are various types of hybridisations involving *s*, *p* and *d*-type of orbitals. The type of hybridisation gives the characteristic shape of the molecule or ion.

Answer the following questions :

D1. Which of the following statement is not correct ?
(*a*) The hybridised orbitals are always equivalent in energy and shape.
(*b*) *sp* hybridised orbitals has more *s*-character than sp^2 hybridised orbital.
(*c*) Promotion of electron is essential condition prior to hybridisation.
(*d*) The hybridized orbitals are directed in space in some preferred directions to have minimum repulsion between electron pairs.

D2. Which other molecule or ion has same shape as NO_2^+ ion ?
(*a*) SF_2 (*b*) H_3O^+
(*c*) XeF_2 (*d*) CO_3^{2-}

D3. Which of the following has correct placement of lone pairs and bond pairs ?

(*a*) 
(*b*) 
(*c*) 
(*d*) 

D4. Which molecule does not have the same type of hybridisation as P has in PF_5?
(*a*) ClF_3 (*b*) SF_4
(*c*) XeF_4 (*d*) XeF_2

D5. Which of the following molecule / ion does not have same number of lone pairs ?
(*a*) SF_4 (*b*) PH_3
(*c*) ClO_3^- (*d*) XeF_2

Passage II

Molecular orbital theory as developed by Hund and Mulliken concerns with the formation of molecular orbitals formed by linear combination of atomic orbitals. The electrons are present in these molecular orbitals. The molecular orbitals are filled exactly in the same way as atomic orbitals are filled. The molecular orbital configuration helps us to calculate bond order which gives information about the number of bonds present between atoms. The bond order is related to bond length and bond strength.

Answer the following questions :

D6. Which of the following combination does not give σ MO (assume Z-axis as internuclear axis)
(*a*) $2p_x + 2p_x$ (*b*) $2p_z + 2s$
(*c*) $2s + 2s$ (*d*) $2p_z + 2p_z$

D7. Which one of the following does not have single electron in a bonding molecular orbital?
(*a*) CN (*b*) B_2
(*c*) NO (*d*) N_2^+

D8. Which of the following MO has highest energy in a molecular orbital energy diagram or N_2 molecule?
(*a*) σ*2s (*b*) σ2*pz*
(*c*) π2*px* (*d*) σ2*s*

Answers

Passage I. D1. (*c*) **D2.** (*c*) **D3.** (*b*) **D4.** (*c*) **D5.** (*d*)
Passage II. D6. (*a*) **D7.** (*c*) **D8.** (*b*)

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D9. Which of the following is expected to have largest bond length ?
(*a*) O_2 (*b*) O_2^+
(*c*) O_2^- (*d*) O_2^{2-}

D10. Which of the following will have maximum number of electrons in antibonding MOs ?
(*a*) N_2^+ (*b*) O_2^+
(*c*) F_2 (*d*) Be_2

Answers

Passage II. D9. (*d*) **D10.** (*c*)

Assertion Reason Type Questions

The questions given below consists of an Assertion and the Reason. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
(*b*) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.
(*c*) If assertion is CORRECT but reason is INCORRECT.
(*d*) If assertion is INCORRECT but reason is CORRECT.
(*e*) If both assertion and reason are INCORRECT.

1. Assertion : Ionic compounds tend to non-volatile.
Reason : The intermolecular forces in these compounds are weak.

2. Assertion : The dipole moment helps to predict whether a molecule is polar or non-polar.
Reason : The dipole moment helps to predict the geometry of molecules.

3. Assertion : BF_3 molecule is planar while NF_3 is pyramidal.
Reason : N atom is smaller than B atom.

4. Assertion : CO_2 is non-polar while H_2O is polar, though both are triatomic.
Reason : CO_2 is linear while H_2O is angular.

5. Assertion : NO_3^- is plannar while NH_3 is pyramidal.
Reason : N in NO_3^- has sp^2 and in NH_3 has sp^3 hybridisation.

6. Assertion : Both BF_3 and PF_5 do not obey octet rule.
Reason : Both are electron deficient molecules.

7. Assertion : Bond angle in H_2O is less than that in H_2S.
Reason : Electronegativity of O is more than that of S.

8. Assertion : C_2H_2 molecule is linear.
Reason : In C_2H_2 carbon atoms remain unhybridized.

9. Assertion : *cis* 1, 2-dichloroethane has no dipole moment.
Reason : Two C–Cl bonds cancel the bond polarity of each other.

10. Assertion : Covalent bonds are rigid and directional.
Reason : Covalent compounds undergo molecular reactions which are very slow.

11. Assertion : Though the central atoms of both NH_3 and H_2O molecules are sp^3 hydridised, yet H–N–H bond angle is greater than that of H–O–H.
Reason : This is because nitrogen atom has one lone pair and oxygen atom has two lone pairs.
(NCERT Exemplar Problem)

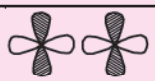
12. Assertion : Among two O–H bonds in H_2O molecule, the energy required to break the first O–H bond and the other O–H bond is the same.
Reason : This is because the electronic environment around oxygen is the same even after breakage of one O–H bond.
(NCERT Exemplar Problem)

Answers

1. (*c*) **2.** (*a*) **3.** (*b*) **4.** (*a*) **5.** (*a*) **6.** (*c*) **7.** (*d*) **8.** (c) **9.** (*e*) **10.** (*b*)
11. (*a*) **12.** (*e*)

Matching Type Questions

1. Match the orbital overlap figures shown in List-I with the description given in List-II and select the correct answer using the code given below the lists.

List-I	List-II
(P) 	1. $p-d\pi$ antibonding
(Q)	2. $d-d$ σ bonding
(R)	3. $p-d$ π bonding
(S)	4. $d-d$ σ antibonding

Code:

	P	Q	R	S
(*a*)	2	1	3	4
(*b*)	4	3	2	1
(*c*)	2	3	1	4
(*d*)	4	1	3	2

(JEE Advance 2014)

Answers

1. (*c*)

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Competition File

2. Match the interhalogen compounds of column-I with the geometry in column II and assign the correct code.

Column-I	Column-II
(P) XX'	(*i*) T-shape
(Q) XX'_3	(*ii*) Pentagonal bipyramidal
(R) XX'_5	(*iii*) Linear
(S) XX'_7	(*iv*) Square-pyramidal (*v*) Tetrahedral

Code:

	(P)	(Q)	(R)	(S)
(*a*)	(*iii*)	(*i*)	(*iv*)	(*ii*)
(*b*)	(*v*)	(*iv*)	(*iii*)	(*ii*)
(*c*)	(*iv*)	(*iii*)	(*ii*)	(*i*)
(*d*)	(*iii*)	(*iv*)	(*i*)	(*ii*)

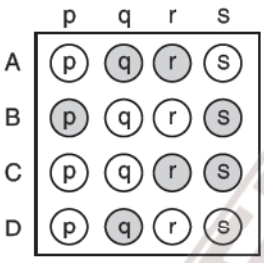
(NEET 2017)

Answers

2. (*a*)

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.



If the correct matches are A-*q*, A-*r*, B-*p*, B-*s*, C-*r*, C-*s* and D-*q*, then the correctly bubbled matrix will look like the following:

1. Match the molecule in Column I with the shape in Column II

Column I	Column II
(A) SF_4	(*p*) Pyramidal
(B) ClF_3	(*q*) Square planar
(C) XeF_4	(*r*) Sea saw
(D) NH_3	(*s*) T-shaped

2. Match the molecule in Column I with the characteristic in Column II

Column I	Column II
(A) O_2^-	(*p*) bond order 2.5 and paramagnetic
(B) N_2	(*q*) bond order 1.5 and paramagnetic
(C) N_2^+	(*r*) bond order 1 and paramagnetic
(D) B_2	(*s*) bond order 3 and diamagnetic

3. Match the molecule in Column I with the characteristic in Column II

Column I	Column II
(A) CO	(*p*) has one lone pair of electrons
(B) SF_4	(*q*) has longer bond length than its unipositive ion
(C) NH_3	(*r*) is paramagnetic
(D) O_2	(*s*) has dipole moment

4. Match the molecule in Column I with the characteristic in Column II

Column I	Column II
(A) B_2	(*p*) paramagnetic
(B) N_2	(*q*) undergoes oxidation
(C) O_2^-	(*r*) undergoes reduction
(D) O_2	(*s*) bond order ≥ 2
	(*t*) mixing of *s* and *p* orbitals

(IIT-JEE 2009)

5. Match the species in Column I with bond order in Column II.

Column I	Column II
(A) NO	(*p*) 1.5
(B) CO	(*q*) 2.0
(C) O_2^-	(*r*) 2.5
(D) O_2	(*s*) 3.0

6. Match the items given in Column I with examples given in Column II.

Column I	Column II
(A) Hydrogen bond	(*p*) C
(B) Resonance	(*q*) LiF
(C) Ionic solid	(*r*) HF
(D) Covalent solid	(*s*) O_3

Answers

1. : (A) – (*r*) (B) – (*s*) (C) – (*q*) (D) – (*p*)
2. (A) – (*q*) (B) – (*s*) (C) – (*p*) (D) – (*r*)
3. : (A) – (*q*), (*s*) (B) – (*p*) (C) – (*p*) (D) – (*q*), (*r*)
4. (A) – (*p*), (*r*), (*t*) (B) – (*s*), (*t*) (C) – (*p*), (*q*), (D) – (*p*), (*q*),(*s*)
5. : (A) – (*r*) (B) – (*s*) (C) – (*p*) (D) – (*q*)
6. (A) – (*r*), (B) – (*s*) (C) – (*q*) (D) – (*p*)

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Competition File

Integer Type Questions

The answer to each of the following questions is a **single digit integer** ranging from 0 to 9.

1. The number of molecules or ions having bond order 2.5 among O_2^+, CN, NO, N_2^+, CO^+, NO^+, O_2^-, CN^-, N_2; is
2. Total number of molecular orbitals occupying one or two electrons in O_2^+ is
3. Total number of coordinate bonds present in $CuSO_4.5H_2O$ is
4. Total number of electrons present in πMOs in B_2 molecule is
5. The number of molecules having more than one lone pair among the following :
   XeF_4, ClF_3, NH_3, SF_4, XeF_2, BrF_5, H_2O
6. Number of molecules having dipole moment among: BF_3, H_2O, NF_3, H_2S, CO_2, trans-1, 2-dichloroethene, CH_3Cl, CCl_4, HI is
7. The number of molecules in which all atoms donot obey octet rule among the following :
   BeH_2, LiCl, PCl_3, SF_2, BF_3, IF_7, SO_2, XeF_2, PCl_5, H_2SO_4
8. $COCl_2$ is a poisonous gas. The formal charge on O atom is
9. The number of 90° bond angles present in SF_4 molecule is
10. Total number of lone pairs present in the structure of HNO_3 is
11. Based on VSEPR theory, the number of 90 degree F–B–F angles in BrF_5 is *(I.I.T. 2010)*
12. A list of species having the formula XZ_4 is given below:
    XeF_4, SF_4, SiF_4, BF_4^-, BrF_4^-, $[Cu(NH_3)_4]^{2+}$, $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$ and $[PtCl_4]^{2-}$. Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is
    (JEE Advance 2014)
13. Among the triatomic molecules/ions, $BeCl_2$, N_3^-, N_2O, NO_2^+, O_3, SCl_2, ICl_2^-, I_3^- and XeF_2, total number of linear molecule(s)/ion(s) where the hydridization of the central atom does not have contribution from the *d*-orbital(s) is [Atomic number : S = 16, Cl = 17, I = 53 and Xe = 54] *(JEE Advance 2015)*
14. Among H_2, He_2^+, Li_2, Be_2, B_2, C_2, N_2, O_2^- and F_2, the number of diamagnetic species is (Atomic numbers: H =1, He = 2, Li = 3, Be = 4, B = 5, C = 6, N = 7, O = 8, F = 9). *(JEE Advance 2017)*
15. The sum of the number of lone pairs of electrons on each central atom in the following species is
    $[TeBr_6]^{2-}$, $[BrF_2]^+$, SNF_3, and $[XeF_3]^-$
    (Atomic numbers: N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54). *(JEE Advance 2017)*

Answers

1. (4) **2.** (8) **3.** (4) **4.** (2) **5.** (4) **6.** (5) **7.** (6) **8.** (0) **9.** (0) **10.** (7)
11. (0) **12.** (4) **13.** (4) **14.** (6) **15.** (6)

NCERT Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

1. Isostructural species are those which have the same shape and hybridisation. Among the given species identify the isostructural pairs.
   (*a*) [NF_3 and BF_3] (*b*) [BF_4^- and NH_4^+]
   (*c*) [BCl_3 and $BrCl_3$] (*d*) [NH_3 and NO_3^-]
2. Polarity in a molecule and hence the dipole moment depends primarily on electronegativity of the constituent atoms and shape of a molecule. Which of the following has the highest dipole moment ?
   (*a*) CO_2 (*b*) HI
   (*c*) H_2O (*d*) SO_2
3. The types of hybrid orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are expected to be
   (*a*) *sp*, sp^3 and sp^2 (*b*) *sp*, sp^2 and sp^3
   (*c*) sp^2, *sp* and sp^3 (*d*) sp^2, sp^3 and *sp*
4. Hydrogen bonds are formed in many compounds e.g., H_2O, HF, NH_3. The boiling point of such compounds depends to a large extent on the strength of hydrogen bond and the number of hydrogen bonds. The correct decreasing order of the boiling points of H_2O, HF and NH_3 is :
   (*a*) $HF > H_2O > NH_3$ (*b*) $H_2O > HF > NH_3$
   (*c*) $NH_3 > HF > H_2O$ (*d*) $NH_3 > H_2O > HF$

Answers

1. (*b*) **2.** (*c*) **3.** (*b*) **4.** (*b*)

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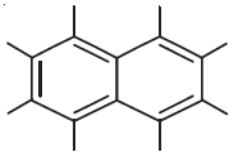
5. In PO_4^{3-} ion the formal charge on the oxygen atom of P–O bond is
(a) + 1 (b) – 1
(c) – 0.75 (d) + 0.75

6. In NO_3^- ion, the number of bond pairs and lone pairs of electrons on nitrogen atom are
(a) 2, 2 (b) 3, 1
(c) 1, 3 (d) 4, 0

7. Which of the following species has tetrahedral geometry ?
(a) BH_4^- (b) NH_2^-
(c) CO_3^{2-} (d) H_3O^+

8. Number of π bonds and σ bonds in the following structure is :



(a) 6, 19 (b) 4, 20
(c) 5, 19 (d) 5, 20

9. Which of the following molecule/ion does not contain unpaired electrons ?
(a) N_2^+ (b) O_2
(c) O_2^{2-} (d) B_2

10. In which of the following molecule/ion all the bonds are not equal ?
(a) XeF_4 (b) BF_4^-
(c) C_2H_4 (d) SiF_4

11. In which of the following substances will hydrogen bond be strongest ?
(a) HCl (b) H_2O
(c) HI (d) H_2S

12. If the electronic configuration of an element is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$, the four electrons involved in chemical bond formation will be _____.
(a) $3p^6$ (b) $3p^6, 4s^2$
(c) $3p^6, 3d^2$ (d) $3d^2, 4s^2$

13. Which of the following angle corresponds to sp^2 hybridisation ?
(a) 90° (b) 120°
(c) 180° (d) 109°

The electronic configurations of three elements, A, B and C are given below. Answer the questions 14 to 17 on the basis of these configurations.

A	$1s^2$	$2s^2$	$2p^6$		
B	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^3$
C	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^5$

14. Stable form of A may be represented by the formula :
(a) A (b) A_2
(c) A_3 (d) A_4

15. Stable form of C may be represented by the formula :
(a) C (b) C_2
(c) C_3 (d) C_4

16. The molecular formula of the compound formed from B and C will be
(a) BC (b) B_2C
(c) BC_2 (d) BC_3

17. The bond between B and C will be
(a) ionic (b) covalent
(c) hydrogen (d) coordinate

18. Which of the following order of energies of molecular orbitals of N_2 is correct ?
(a) $(\pi 2p_y) < (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(b) $(\pi 2p_y) > (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(c) $(\pi 2p_y) > (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(d) $(\pi 2p_y) > (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$

19. Which of the following statement is not correct from the view point of molecular orbital theory ?
(a) Be_2 is not a stable molecule.
(b) He_2 is not stable but He_2^+ is expected to exist.
(c) Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules belonging to the second period.
(d) The order of energies of molecular orbitals in N_2 molecule is

$$\sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

20. Which of the following options represents the correct bond order :
(a) $O_2^- > O_2 > O_2^+$
(b) $O_2^- < O_2 < O_2^+$
(c) $O_2^- > O_2 < O_2^+$
(d) $O_2^- < O_2 > O_2^+$

21. The electronic configuration of the outermost shell of the most electronegative element is
(a) $2s^2 2p^5$ (b) $3s^2 3p^5$
(c) $4s^2 4p^5$ (d) $5s^2 5p^5$

22. Amongst the following elements whose electronic configurations are given below, the one having the highest ionisation enthalpy is
(a) $[Ne]3s^2 3p^1$ (b) $[Ne]3s^2 3p^3$
(c) $[Ne]3s^2 3p^2$ (d) $[Ar]3d^{10} 4s^2 4p^3$

Answers

5. (c) **6.** (d) **7.** (a) **8.** (c) **9.** (c) **10.** (c) **11.** (b) **12.** (d) **13.** (b) **14.** (a)
15. (b) **16.** (d) **17.** (b) **18.** (a) **19.** (d) **20.** (b) **21.** (a) **22.** (b)

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Multiple Choice Questions (Type-II)

23. Which of the following have identical bond order ?
(*a*) CN^- (*b*) NO^+
(*c*) O_2^+ (*d*) O_2^{2-}

24. Which of the following attain the linear structure :
(*a*) $BeCl_2$ (*b*) NCO^+
(*c*) NO_2 (*d*) CS_2

25. CO is isoelectronic with
(*a*) NO^+ (*b*) N_2
(*c*) $SnCl_2$ (*d*) NO_2^-

26. Which of the following species have the same shape ?
(*a*) CO_2 (*b*) CCl_4
(*c*) O_3 (*d*) NO_2^-

27. Which of the following statements are correct about CO_3^{2-} ?
(*a*) The hybridisation of central atom is sp^3.
(*b*) Its resonance structure has one C–O single bond and two C=O double bonds.
(*c*) The average formal charge on each oxygen atom is 0.67 units.
(*d*) All C–O bond lengths are equal.

28. Which among the following are diamagnetic ?
(*a*) N_2 (*b*) N_2^{2-}
(*c*) O_2 (*d*) O_2^{2-}

29. Species having same bond order are :
(*a*) N_2 (*b*) N_2^-
(*c*) F_2^+ (*d*) O_2^-

30. Which of the following statements are not correct ?
(*a*) NaCl being an ionic compound is a good conductor of electricity in the solid state.
(*b*) In canonical structures, there is a difference in the arrangement of atoms.
(*c*) Hybrid orbitals form stronger bonds than pure orbitals.
(*d*) VSEPR theory can explain the square planar geometry of XeF_4.

Answers

23. (*a*, *b*) **24.** (*a*, *d*) **25.** (*a*, *b*) **26.** (*c*, *d*) **27.** (*c*, *d*) **28.** (*a*, *d*) **29.** (*c*, *d*) **30.** (*a*, *b*)

Matching Type Questions

31. Match the species in Column I with the type of hybrid orbitals in Column II.

Column I	*Column II*
(*i*) SF_4	(*a*) sp^3d^2
(*ii*) IF_5	(*b*) d^2sp^3
(*iii*) NO_2^+	(*c*) sp^3d
(*iv*) NH_4^+	(*d*) sp^3
	(*e*) sp

32. Match the species in Column I with the geometry/ shape in Column II.

Column I	*Column II*
(*i*) H_3O^+	(*a*) Linear
(*ii*) HC ≡ CH	(*b*) Angular
(*iii*) ClO_2^-	(*c*) Tetrahedral
(*iv*) NH_4^+	(*d*) Trigonal bipyramidal
	(*e*) Pyramidal

33. Match the species in Column I with the bond order in Column II.

Column I	*Column II*
(*i*) NO	(*a*) 1.5
(*ii*) CO	(*b*) 2.0
(*iii*) O_2^-	(*c*) 2.5
(*iv*) O_2	(*d*) 3.0

34. Match the items given in Column I with examples given in Column II.

Column I	*Column II*
(*i*) Hydrogen bond	(*a*) C
(*ii*) Resonance	(*b*) LiF
(*iii*) Ionic solid	(*c*) H_2
(*iv*) Covalent solid	(*d*) HF
	(*e*) O_3

35. Match the shape of molecules in Column I with the type of hybridisation in Column II.

Column I	*Column II*
(*i*) Tetrahedral	(*a*) sp^2
(*ii*) Trigonal	(*b*) sp
(*iii*) Linear	(*c*) sp^3

Answers

31. (*i*) – (*c*); (*ii*) – (*a*); (*iii*) – (*e*); (*iv*) – (*d*)
32. (*i*) – (*e*); (*ii*) – (*a*); (*iii*) – (*b*); (*iv*) – (*c*)
33. (*i*) – (*c*); (*ii*) – (*d*); (*iii*) – (*a*); (*iv*) – (*b*)
34. (*i*) – (*d*); (*ii*) – (*e*); (*iii*) – (*b*); (*iv*) – (*a*)
35. (*i*) – (*c*); (*ii*) – (*a*); (*iii*) – (*b*)

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Assertion and Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below :

(*a*) A and R both are correct and R is the correct explanation of A.

(*b*) A and R both are correct but R is not the correct explanation of A.

(*c*) A is true but R is false.

(*d*) A and R both are false.

36. Assertion (A) : Sodium chloride formed by the action of chlorine gas on sodium metal is a stable compound.
Reason (R) : This is because sodium and chloride ions acquire octet in sodium chloride formation.

37. Assertion (A) : Though the central atom of both NH_3 and H_2O molecules are sp^3 hydridised, yet H–N–H bond angle is greater than that of H–O–H.
Reason (R) : This is because nitrogen atom has one lone pair and oxygen atom has two lone pairs.

38. Assertion (A) : Among the two O–H bonds in H_2O molecule, the energy required to break the first O–H bond and the other O–H bond is the same.
Reason (R) : This is because the electronic environment around oxygen is the same even after breakage of one O–H bond.

Answers

36. (*a*) **37.** (*a*) **38.** (*d*)

MCQ Based on Given Comprehension

Comprehension given below is followed by some multiple choice questions. Each question has one correct option. Choose the correct option.

Molecular orbitals are formed by the overlap of atomic orbitals. Two atomic orbitals combine to form two molecular orbitals called bonding molecular orbital (BMO) and anti-bonding molecular orbital (ABMO). Energy of anti-bonding orbital is raised above the parent atomic orbitals that have combined and the energy of the bonding orbital is lowered than the parent atomic orbitals. Energies of various molecular orbitals for elements hydrogen to nitrogen increase in the order : $\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < (\pi 2p_x \approx \pi 2p_y) < \sigma 2p_z < (\pi^*2p_x \approx \pi^*2p_y) < \sigma^*2p_z$ and for oxygen and fluorine order of energy of molecular orbitals is given as : $\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < \sigma 2p_z < (\pi 2p_x \simeq \pi 2p_y) < (\pi^*2p_x \simeq \pi^*2p_y) < \sigma^*2p_z$. Different atomic orbitals of one atom combine with those atomic orbitals of the second atom which have comparable energies and proper orientation. Further, if the overlapping is head on, the molecular orbital is called '*pi*', (π). The molecular orbitals are filled with electrons according to the same rules as followed for filling of atomic orbitals. However, the order for filling is not the same for all molecules or their ions. Bond order is one of the most important parameters to compare the strength of bonds.

39. Which of the following statements is correct ?

(*a*) In the formation of dioxygen from oxygen atoms 10 molecular orbitals will be formed.

(*b*) All the molecular orbitals in the dioxygen will be completely filled.

(*c*) Total number of bonding molecular orbitals will not be same as total number of anti-bonding orbitals in dioxygen.

(*d*) Number of filled bonding orbitals will be same as number of filled anti-bonding orbitals.

40. Which of the following molecular orbitals has maximum number of nodal planes ?

(*a*) σ^*1s (*b*) σ^*2p_z

(*c*) $\pi 2p_x$ (*d*) π^*2p_y

41. Which of the following pair is expected to have the same bond order ?

(*a*) O_2, N_2 (*b*) O_2^+, N_2^-

(*c*) O_2^-, N_2^+ (*d*) O_2^-, N_2^-

42. In which of the following molecules, $\sigma 2p_z$ molecular orbital is filled after $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals ?

(*a*) O_2 (*b*) Ne_2

(*c*) N_2 (*d*) F_2

Answers

39. (*a*) **40.** (*d*) **41.** (*b*) **42.** (*c*)

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Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A3. (*a*): Because of small size of Li^+.

A5. (*c*): $\mu_{ionic} = q \times d$

$= 4.8 \times 10^{-10}$ e.s.u. $\times 1.275 \times 10^{-8}$ cm

$= 6.12 \times 10^{-18}$ e.s.u. cm = 6.12 D

% Ionic character

$$= \frac{\text{Observed dipole moment}}{\text{Dipole moment for complete ionic character}} \times 100$$

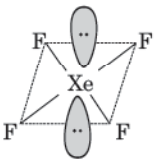
$$= \frac{1.03}{6.12} \times 100 = 16.83\%$$

A8. (*d*): Al^{3+} has maximum polarising power because of small size and high charge.

A10. (*c*): Bond angles are H_2O (104.5°), NH_3 (107°), CH_4 (109.5°) and CO_2 (180°).

A17. (*a*): NO_2^+ has linear geometry and therefore bond angle is highest (180°).

A19. (*d*): In XeF_4, there are two lone pairs.



A24. (*b*): O_2^- : KK $(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^*2p_x)^2(\pi^*2p_y)^1$

$$\text{B.O.} = \frac{8-5}{2} = 1.5$$

A28. (*c*): NO : $KK(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p_x})^2(\pi_{2p_y})^2(\sigma_{2p_z})^2(\pi^*_{2p_x})^1$

$$\text{B.O.} = \frac{8-3}{2} = 2.5$$

(*i*) $\text{B.O.}(NO^-) = \frac{8-4}{2} = 2$

(*ii*) $\text{B.O.}(NO^+) = \frac{8-2}{3} = 3$

(*iii*) B.O. (NO) = 2.5

(*iv*) $\text{B.O.}(NO^{2+}) = \frac{7-2}{2} = 2.5$

(*v*) $\text{B.O.}(NO^{2-}) = \frac{8-5}{2} = 1.5$

$\therefore$ Correct order is : (*v*) < (*i*) < (*iv*) = (*iii*) < (*ii*)

A29. (*d*): Only O_2^{2-} has all electrons paired and is diamagnetic. All other are paramagnetic.

A30. (*a*): Bond orders are O_2^+ (2.5), O_2 (2.0), O_2^- (1.5) and O_2^{2-} (1.0). So, O_2^+ has maximum bond strength.

A34. (*b*): HCl has lowest boiling point.

A35. (*d*): Water has maximum density at 277K.

B. *mcq from competitive examinations*

B2. (*b*) : AB_5 molecules may have square pyramidal or trigonal bipyramidal geometry.

B3. (*a*): Both BrO_3^- and XeO_3 involve sp^3 hybridisation of central atom and has one lone pair of electrons. These have pyramidal shape.

B4.(*a*): The correct order of CO bond length will be

$CO < CO_2 < CO_3^{2-}$

B6. (*c*): BF_3: sp^2, NO_2^-:sp^2, NH_2^-:sp^3, H_2O:sp^3

B7. (*a*): $Sb\,Cl_5^{2-}$ is sp^3d^2 while all other molecules/ions in the question involve sp^3 *d* hybridisation.

B8. (*d*) : Bond order of Be_2 is zero, so it does not exist.

B9. (*b*) Shapes are : SO_2(angular), SF_4(see saw), ClF_3(T-shaped), BrF_5(square pyramidal), XeF_4(square planar).

B10. (*a*) : Bond order of O_2^+ is maximum 2.5 and hence minimum bond length.

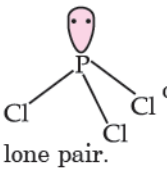
B11. (*a*) : The hybridizations are :

$NO_2^-(sp^2)$, $NO_3^-(sp^2)$, $NH_2^-(sp^3)$, $NH_4^+(sp^3)$ $SCN^-(sp)$.

NO_2^- and NO_3^- have same hybridisation.

B12. (*a*) : O_2^{2-} and B_2 have bond order equal to 1.

B13. (*d*) :

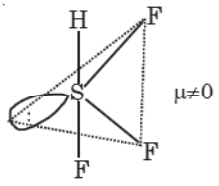


contains three bond pairs and one lone pair.

B14. (*d*) : BF_4^- and NH_4^+ involve sp^3 hybridisation and are tetrahedral.

B15. (*b*) : O_2^- : KK $(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^*2p_x)^2(\pi^*2p_y)^1$; Bond order = $\frac{8-5}{2} = 1.5$ pyramidal.

B16. (*d*) : SF_4 has see saw shape involving sp^3d hybridisation. It has four bond pairs and one lone pair.



B17. (*d*) : O_2^- : KK$(\sigma 2s)^2$ $(\sigma^*2s)^2$ $(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^*2p_x)^2(\pi^*2p_y)^1$

It has one unpaired electron and hence is paramagnetic.

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B18. (*d*) : H_2O does not contain any π bond.

B21. (*b*) : NO_3^- has plane triangular shape.

B22. (*b*) : SF_4, NH_3 and O_3 have one lone pair of electrons on the central atom.

B23. (*b*) : SF_4 has see saw shape and not tetrahedral.

B24. (*c*) :

Species	Bond order	Magnetic character
F_2	1	Diamagnetic
O_2	2	Paramagnetic
N_2	3	Diamagnetic
O_2^{2-}	1	Diamagnetic
Li_2	1	Diamagnetic
B_2	1	Paramagnetic

He and Ne are monoatomic and diamagnetic.

So, Li_2 and B_2 have same bond order, and diamagnetic and paramagnetic properties.

B25. (*c*) : The bond order of the species are:

$O_2^+ (2.5) > O_2 (2) > O_2^- (1.5) > O_2^{2-} (1)$

Thus, the order of stability is same as above.

B26. (*b*) : XeF_4 has square planar geometry and XeO_4 has tetrahedral geometry.

B27. (*b*) : SO_3^{2-} and ClO_3^- have same number of electrons (42) and same pyramidal shape.

B28. (*b*) : $O_2^- (1.5) < O_2^+ (2.5) < O_2^{2+} (3.0)$

B29. (*a*) : NO_2^+ is linear and bond angle of 180°.

B30. (*d*) : Bond angles in CH_4, NH_3 and H_2O are:

$CH_4 = 109.5°$, $NH_3 = 107°$ and $H_2O = 104.5°$

Statement (*d*) is wrong because bond angle of H_2O is smaller than that of NH_3.

B33. (*d*) : In XeF_4, the hybridisation is sp^3d^2 and geometry is square planar with two positions occupied by lone pairs.

B35. (*b*) : IBr_2^- and XeF_2 are isostructural (linear shape) and central atoms (I^- and Xe) of both contain same number of valence electrons.

B36. (*c*) : BCl_3 has trigonal planar structure and bond angle is 120°.

B37. (*b*) : CN^- and CO have same bond order of 3.

B38. (*a*) : Smaller the size of cation, more will be its polarising power. Hence, BeH_2 is least ionic.

$$BeH_2 < CaH_2 < BaH_2$$

B39. (*b*) : NO: KK $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2$

$$= (\pi 2p_y)^2(\sigma 2p_z)^2(\pi^* 2p_x)^1$$

$$\text{B.O.} = \frac{8-3}{2} = 2.5$$

$$CN^- : KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2(\sigma 2p_z)^2$$

$$\text{B.O.} = \frac{8-2}{2} = 3$$

$$CN : KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2(\sigma 2p_z)^1$$

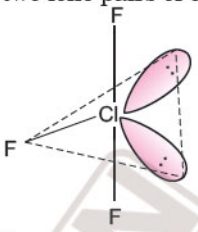
$$\text{B.O.} = \frac{7-2}{2} = 2.5$$

$$CN^+ : KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2$$

$$\text{B.O.} = \frac{6-2}{2} = 2$$

Hence CN^- has highest bond order.

B40. (*b*) : ClF_3 has two lone pairs of electrons on Cl atom.



B41. (*d*) : O_2^{2-} is diamagnetic.

B42. (*a*) : F—H.....F is the strongest hydrogen bond because of largest electronegativity difference between H and F.

B43. (*b*): NO^+ and CN^- are isoelectronic and have same bond order of 3.

B45. (*a*): The bond moments para to each other cancel due to their opposite directions. The other two groups are meta to each other at an angle of 120°.

$$\therefore \quad \text{Dipole moment, } \mu = \sqrt{\mu_2^1 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

where $\mu_1 = \mu_2 = 1.5$ D

$$\therefore \quad \mu = \sqrt{(1.5)^2 + (1.5)^2 + 2(1.5)(1.5)\cos 120^\circ} = 1.5 \text{ D}$$

B47. (*c*) : In BF_3, hybridisation of B is sp^2 and its geometry is trigonal planar. In BF_4^-, the hybridisation of B is sp^3 and its geometry is tetrahedral.

B51. (*c*) : No. of lone pairs : $XeF_4(2)$, $XeF_6(1)$, $XeO_3(1)$, $XeF_2(3)$.

B52. (*d*) : Calcium carbide is an ionic carbide having the structure :

$$Ca^{2+}(C \equiv C)^{2-}$$

It contains one sigma and two *pi* bonds.

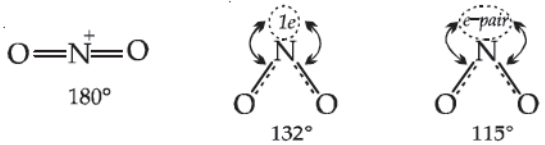
B53. (*c*) : In $POCl_3$, the hybridization is sp^3 and number of lone pair = 0

B54. (*a*) : B_2 : KK $(\sigma 2s)^2$ $(\sigma^* 2s)^2$ $(\pi 2p_x)^1$ $(\pi 2p_y)^1$

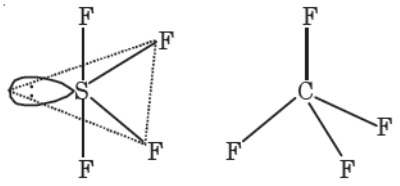
B56. (*b*) : PF_5 is trigonal bipyramidal and BrF_5 is square

B57. (*b*) : NO_2^+ is linear molecule having bond angle of 180°.

NO_2 has one unshared electron while NO_2^- has a lone pair of electrons. Therefore, lone pair causes more repulsion than unshared electron and therefore, bond angle is forced closer.



B58. (*d*) :



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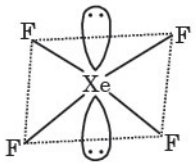
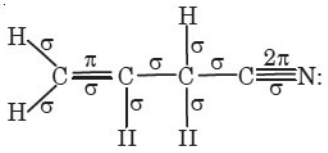


(lone pair = 2)

Hence, all have different shapes with 1, 0 and 2 lone pairs.

B59. (*b*) : 

Allyl cyanide

$\sigma = 9$, $\pi = 3$, lone pair = 1.

B60. (*d*) : $H_2^{2+} : (\sigma 1s)^0$

Bond order = 0

$He_2 : (\sigma 1s)^2(\sigma^*1s)^2$

Bond order $\frac{2-2}{2} = 0$

Hence, He_2^{2+} and He_2 have zero bond order.

B61. (*c*) : Stability depends upon bond order.

$Li_2 : KK(\sigma 2s)^2$: Bond order = 1

$Li_2^+ : KK(\sigma 2s)^1$: Bond order = $\frac{1}{2}$

$Li_2^- : KK(\sigma 2s)^2(\sigma^*2s)^1$: Bond order = $\frac{1}{2}$

Li_2^+ is more stable than Li_2^- because it has less number of antibonding electrons. Hence,

$$Li_2^- < Li_2^+ < Li_2$$

B63. (*c*) : The position of bond pairs of electrons in N–F bond is away from N than the position of bond pairs in N–H bonds. Therefore, the force of repulsion between the bonded pairs of electrons in NF_3 is less than that in NH_3. Hence, the larger lone pair-bond pair repulsion forces the bonded electron pairs to come closer to each other in NF_3 and bond angle is less in comparison to that in NH_3.

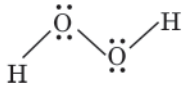
B65. (*b*) SF_4 has see-saw (distorted trigonal bipyramidal) shape.

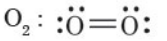
B66. (*c*) Both XeF_2 and $ZnCl_2$ are linear molecules.

B68. (*b*) NO is paramagnetic in gaseous state due to presence of one unpaired electron.

B69. (*a*) H_2O : *l*.p = 2, $SnCl_2$: *l*.p. = 1,

PCl_3 : *l*.p. = 1, XeF_2 : *l*.p. = 3

B70. (*b*) H_2O_2 :  Bond order = 1

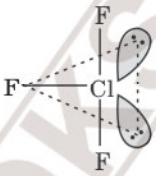
O_2 :  Bond order = 2

O_3 :

Bond order between 1 and 2; approximately 1.5

$\therefore$ Bond length is $H_2O_2 > O_3 > O_2$

B71. (*d*) ClF_3 has T-shape

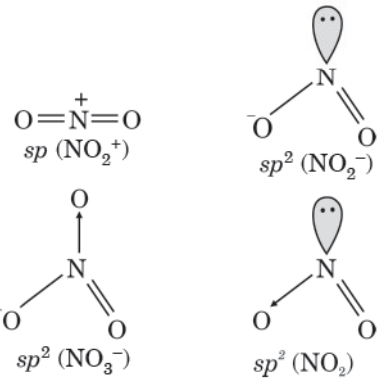


B72. (*b*) F ⟷ Be ⟷ F. The opposite bond dipoles cancel each other and the resulting dipole moment is zero.

B73. (*d*) Bond orders are :

O_2^{2-} (1), O_2^- (1.5), O_2 (2), O_2^+ (2.5)

B75. (*a*)



N in NO_2^+ is *sp* hybridised.

B76. (*a*): B_2 : $KK\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\pi 2p_x)^1 = (\pi 2p_y)^1$

Two unpaired electrons and hence paramagnetic.

C_2 : $KK\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\pi 2p_x)^2 = (\pi 2p_y)^2$

No unpaired electron and hence diamagnetic.

B77. (*d*): A molecule with 3 bond pairs and 1 lone pair of electrons like NH_3 is pyramidal.

B78. (*d*): $:N \equiv \overset{+}{N} - \ddot{O}:^-$ is the correct electron dot structure.

B80. (*a*): CN^- : $KK\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\pi 2p_x)^2 = (\pi 2p_y)^2\,(\sigma 2p_z)^2$

$$\text{B.O.} = \frac{8-2}{2} = 3$$

NO^+ : $KK\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\pi 2p_x)^2 = (\pi 2p_y)^2\,(\sigma 2p_z)^2$

$$\text{B.O.} = \frac{8-2}{2} = 3$$

O_2^- : $KK(\sigma 2s)^2\,(\sigma^*2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^*2p_x)^2\,(\pi^*2p_y)^1$

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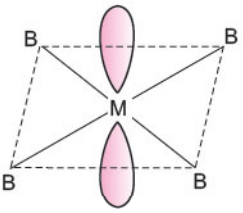
$$\text{B.O.} = \frac{8-5}{2} = 1.5$$

CN^- and NO^+ have same bond order.

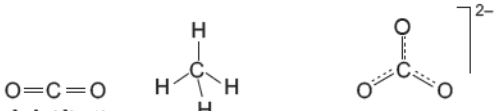
B81. (*b*): CO is diamagnetic while all other : O_2, B_2 and NO are paramagnetic.

B82. (*a*): The structure will be octahedral with two lone pairs.



The geometry is square planar.

B86. (*c*):



B87. (*d*):

He_2^{2+} $(\sigma 1s)^2$ $\text{B.O.} = \frac{2-0}{2} = 1$

He_2^{+} $(\sigma 1s)^2(\sigma^* 1s)^1$ $\text{B.O.} = \frac{2-1}{2} = 0.5$

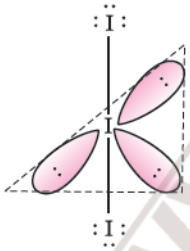
H_2^{-} $(\sigma 1s)^2(\sigma^* 1s)^1$ $\text{B.O.} = \frac{2-1}{2} = 0.5$

H_2^{2-} $(\sigma 1s)^2(\sigma^* 1s)^2$ $\text{B.O.} = \frac{2-2}{2} = 0$

H_2^{2-} is not viable molecule because bond order is zero.

B88. (*c*): KCl has only ionic bond.

B89. (*c*):



No. of lone pairs = 9

B90. (*d*): Li_2 : $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2$

Li_2^+ : $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^1$

$\text{Bond order} = \frac{3-2}{2} = \frac{1}{2}$

Li_2^- : $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^1$

$\text{Bond order} = \frac{4-3}{2} = \frac{1}{2}$

Both have bond order of 0.5 and are stable.

B91. (*b*):

(*a*) $N_2 \longrightarrow N_2^+$ B.O : 3 $\longrightarrow$ 2.5; Dia $\longrightarrow$ Para

(*b*) $NO \longrightarrow NO^+$ B.O : 2.5 $\longrightarrow$ 3; Para $\longrightarrow$ Dia

(*c*) $O_2 \longrightarrow O_2^-$ B.O : 2 $\longrightarrow$ 1; Para $\longrightarrow$ Dia

(*d*) $O_2 \longrightarrow O_2^+$ B.O : 2 $\longrightarrow$ 2.5; Para $\longrightarrow$ Para

B92. (*a*):

(*a*) N_2^+ : $(KK)(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^1$

$\text{B.O} = \frac{7-2}{2} = 2.5,\ 2\pi \text{ and } \frac{1}{2}\sigma$

(*b*) N_2 : $(KK)(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2$

$\text{B.O} = \frac{8-2}{2} = 3;\ 2\pi \text{ and } 1\sigma$

(*c*) O_2 : $KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1$ $(\pi^* 2p_y)^1$

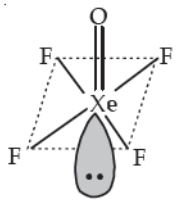
$\text{B.O} = \frac{8-4}{2} = 2;\ 1\pi \text{ and } 1\sigma$

(*d*) O_2^+ : $KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1$

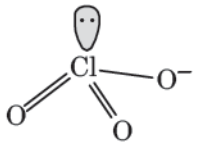
$\text{B.O} = \frac{8-4}{2} = 2;\ 1\pi \text{ and } 1\sigma$

B96. (*a*): NO_3^-: trigonal planar, CO_3^{2-} : trigonal planar, ClO_3^-: pyramidal and SO_3: trigonal planar. NO_3^- and CO_3^{2-} are isoelectronic also.

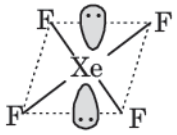
B97. (*b*): $XeOF_4$ involves sp^3d^2 hybridisation and has one lone pair of electrons.



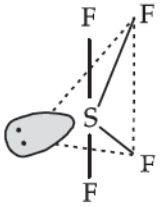
B98. (*d*): I_3^- has maximum number of unpaired electrons.



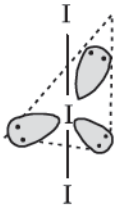
(*a*)



(*b*)



(*c*)



(*d*)

B100. (*c*) : B_2 (10) : $\sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\ \pi 2p_x^1 \pi 2p_y^1$

$\text{Bond order} = \frac{6-4}{2} = 1$

It is paramagnetic.

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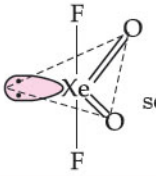
B102. (*d*) : XeO_2F_2 involves sp^3d hybridisation and shape is



see saw.

C. *mcq with more than one correct answer*

C1. (*a,c*) : O_2^- and B_2 are paramagnetic while N_2 and F_2 are diamagnetic.

C2. (*b,c*) : $SnCl_2$ and SF_2 have an gular (or V) shape.

C3. (*a,d*) : B_2 and O_2 are paramagnetic.

C4. (*b,d*) : Promotion is not essential for hybridiation. Resonance has no role in M.O. theory.

C6. (*b,c*) : NH_3 and H_2O involve sp^3 hybridisation.

ClF_3 and PF_5 involve sp^3d hybridisation.

C7. (*c,d*) : ClF_3: T-shape, SF_4 : sea-saw

C9. (*a, b, d*) (*c*) is not correct because HCOOH is stronger acid than CH_3COOH due to inductive effect and not due to hydrogen bonding. All other are correct.

C11. (*a,c*) :(*a*) The M.O. electronic configuration of C_2^{2-} is

$(\sigma 1s)^2\ (\sigma^*1s)^2\ (\sigma 2s)^2\ (\sigma^*2s)^2\ (\pi 2px)^2 = (\pi 2py)^2\ (\sigma 2pz)^2$

It is diamagnetic because there is no unpaired electron.

(*b*) Bond order of O_2^{2+} is 3 and that of O_2 is 2. therefore, bond length of O_2^{2+} is shorter than that of O_2.

(*c*) $N_2^+ : (\sigma 1s)^2\ (\sigma^*1s)^2\ (\sigma 2s)^2\ (\sigma^*2s)^2\ (\pi 2p_x)^2 = (\pi 2p_y)^2\ (\sigma 2p_z)^2$

Bond order of $N_2^+ = \dfrac{9-4}{2} = 2.5$

$N_2^- : (\sigma 1s)^2\ (\sigma^*1s)^2\ (\sigma 2s)^2\ (\sigma^*2s)^2\ (\pi 2p_x)^2 = (\pi 2p_y)^2\ (\sigma 2p_z)^2\ (\pi^*2p_x)^1$

Bond order of $N_2^- = \dfrac{10-5}{2} = 2.5$

N_2^+ and N_2^- have same bond order.

(*d*) He_2^+ has less energy than two isolated He atoms.

C12. (*b,c*) : $O_2^{2-} : (\sigma 1s)^2(\sigma^*1s)^2(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2\ (\pi 2p_y)^2(\pi^*2p_x)^2(\pi^*2p_y)^2$

It is diamagnetic

Bond order = $= \dfrac{10-8}{2} = 1$

D. *mcq based on comprehension*

D1. (*c*) : Promotion is not essential condition prior to hybridisation.

D2. (*c*) : NO_2^+ ion is linear. XeF_2 is also linear.

D3. (*b*) : For minimum repulsion, the lone pairs should be present on equatorial positions.

D4. (*c*) : PF_5, ClF_3, SF_4 and XeF_2 involve sp^3d hybridisation. XeF_4 involves sp^3d^2 hybridisation.

D5. (*d*) : XeF_2 has three lone pairs of electrons while all other have one lone pair of electrons.

D7. (*c*) : NO has single electron in π-antibonding MO.

D8. (*b*) : $\sigma 2p_z$ has highest energy.

D9. (*d*) : O_2^{2-} has smallest bond order (1) and therefore, has longest bond length.

D10. (*c*) : F_2 has maximum number of electrons in anti-bonding MOs.

Matching Type Questions

2. (*a*) : (P) XX′ – (*iii*) Linear

(Q) XX_3' – (*i*) T-shape

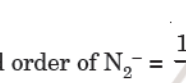
(R) XX_5' – (*iv*) Square pyramidal

(S) XX_7' – (*ii*) Pentagonal bipyramidal

Matrix Match Type Questions

(A) If loss of electron increases bond order, oxidation will be feasible whereas if gain of electron increases bond order, reduction will be feasible. From B_2 to N_2, there is mixing of *s* and *p*-orbitals.

Integer Type Questions

- **1** (4) : O_2^+ CN, NO and N_2^+ have bond order of 2.5.
- **2** (8) : $(\sigma 1s)^2\ (\sigma^*1s)^2\ (\sigma 2s)^2\ (\sigma^*2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^*2p_x)^1$
- **3** (4) : $CuSO_4.5H_2O$ has 4 coordinate bonds.
- **4** (2) : B_2 : KK $(\sigma 2s)^2\ (\sigma^*2s)^2(\pi 2p_x)^1(\pi 2p_y)^1$
- **5** (4) : XeF_4, ClF_3, XeF_2, H_2O
- **6** (5) : H_2O, NF_3, H_2S, CH_3Cl, HI
- **7** (6) : BeH_2, LiCl, BF_3, IF_7, SO_2, PCl_5, H_2SO_4
- **9** (0) : It has distorted geometry because of the presence of lone pair. Therefore, none of the bond angle is of 90°.
- **10** (7) :  No. of lone pairs = 7.
- **11** (0) : There is no F–B–F bond angle of 90°
- **12** (4) : XeF_4, BrF_4^-, $[Cu(NH_3)_4]^{2+}$, $[PtCl_4]^{2-}$ have square planar shape.

  XeF_4 : Square planar, SF_4 : see saw; SiF_4 : tetrahedral, BF_4^- : tetrahedral, BrF_4^- : Square planar; $[Cu(NH_3)_4]^{2+}$: Square planar, $[FeCl_4]^{2-}$: tetrahedral; $[CoCl_4]^{2-}$: tetrahedral $\{PtCl_4]^{2-}$: square planar.
- **13** (4) : The linear molecules and their hybridisation are:

  $BeCl_2$ (*sp*), N_3^- (*sp*), N_2O (*sp*), NO_2^+ (*sp*)

  ICl_2^- (sp^3d), I_3^- (sp^3d), XeF_2 (sp^3d)

  Thus, there are four linear molecules/ions where the hybridisation of central atom does not have the contribution from the *d*-orbitals.
- **14** (6) : Diamagnetic species are : H_2, Li_2, Be_2, C_2, N_2, F_2.

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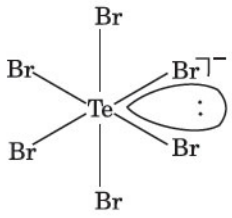
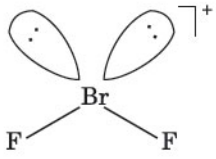
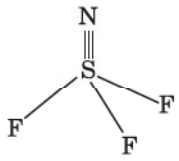
● **15** (6) :



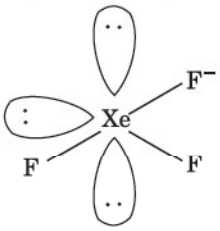
(1 lone pair)



(2 lone pairs)



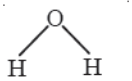
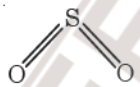
(no lone pair)



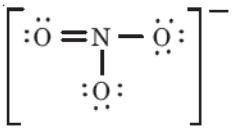
(3 lone pairs)

NCERT Exemplar Problems: MCQ Type-I

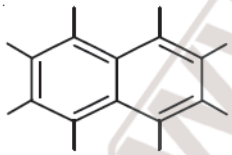
1. (*b*) : NF_3 is pyramidal, BF_3 is planar triangular, BF_4^- and NH_4^+ are tetrahedral.
BCl_3 is triangular planer, $BrCl_3$ is pyramidal, NH_3 is pyramidal, NO_3^- is triangular planar.

2. (*c*) : O=C=O (μ = 0) H—I (μ = 0.38 D)  (μ = 1.84 D)  (μ = 1.62 D)

5. (*c*) : Formal charge on each O atom = $\frac{\text{Total charge}}{\text{No. of O atom}} = -3/4 = -0.75$

6. (*d*)  Bond pairs = 4, lone pair = 0

7. (*a*) : BH_4^- involves sp^3 hybridisation of B and is tetrahedral.

8. (*c*) 
8 C – H, 11 C – C σ bond or 19σ bonds and 5π bonds.

10. (*c*) In C_2H_4, there are two types of bonds C = C and C – H.

11. (*b*) : Only H_2O forms hydrogen bonds.

12. (*d*) : In transition elements, $(n-1)d$ and ns orbitals take part in bond formation.

14. (*a*) : A represents noble gas Ne.

15. (*b*) : C represent Cl atom. Its stable form is Cl_2 *i.e.*, C_2.

16. (*d*) : B represent P and C represents Cl. The stable compound is PCl_3 *i.e.*, BC_3.

17. (*b*) : Both B and C are non-metals and therefore, bond formed between them will be covalent.

18. (*a*) : The order of energies of MOs for N_2 molecule is: $\pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y$

19. (*d*) : $\sigma_{2s} < \sigma^*_{2s} < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma s^* 2p_z$

20. (*b*) : Bond orders : $O_2 = 2.0$, $O_2^+ = 2.5$, $O_2^- = 1.5$
$\therefore \quad O_2^- < O_2 < O_2^+$.

21. (*a*) : The most electronegative element is F having the outermost electronic configuration $2s^2 2p^5$.

NCERT Exemplar Problems: MCQ Type-II

23. (*a*, *b*) Bond orders : $CN^- = 3$, $NO^+ = 3$, $O_2^- = 1.5$, $O_2^{2-} = 1.0$.

24. (*a*, *d*) Both $BeCl_2$ and S = C = S are linear molecules.

25. (*a*, *b*) Electrons in CO = 6 + 8 = 14, $N_2 = 7 + 7 = 14$, $SnCl_2 = 50 + 34 = 84$, $NO_2^- = 7 + 16 + 1 = 24$.

26. (*c*, *d*) Both O_3 and NO_2^- are angular, CO_2 is linear, CCl_4 is tetrahedral.

27. (*c*, *d*) (*a*) The hybridisation is sp^2.
(*b*) In resonance, two C – O bonds and one C = O.
(*c*) Average formal charge on $O = -\frac{2}{3} = -0.67$ units.
(*d*) True : all the bond lengths are equal.

28. (*a*, *d*) Bond N_2 and O_2^{2-} are diamagnetic.

29. (*c*, *d*) Bond orders : $N_2 = 3$, $N_2^- = 2.5$, $F_2^+ = 1.5$, $O_2^+ = 1.5$.

NCERT Exemplar Problems: Comprehensive Questions

39 (*a*) : O_2 : $(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2$ $(\sigma^*_{2s})^2$ $(\sigma_{2p_z})^2$
1 2 3 4 5
$(\pi 2p_x)^2$ $(\pi 2p_y)^2$ $(\pi^*_{2p_x})^1$ $(\pi^*_{2p_y})^1$ σ_{2p_z}
6 7 8 9 10

40. (*d*) : Nodal planes are : $\sigma^*_{1s} = 1$, $\sigma^*_{2p_z} = 1$, $\pi_{2p_x} = 1$, $\pi^*_{2p_y} = 2$.

41. (*b*) : O_2^+ and N_2^- have same bond order (2.5). ($O_2 = 2$, $N_2 = 3$, $O_2^+ = 2.5$, $N_2^- = 2.5$, $O_2^+ = 2.5$, $O_2^- = 1.5$)

42. (*c*) : In N_2, $\sigma 2p_z$ MO is filled after $\pi 2p_x$ and $\pi 2p_y$.

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Unit Practice Test

for Board Examination

Time Allowed : 1 Hr. ***Maximum Marks : 25***

1. Do N_2^+ and O_2^+ have same bond order. (1)

2. Arrange the following bonds in order of increasing ionic character in the molecules :

LiF, K_2O, N_2, SO_2 and ClF_3 (1)

3. Is there any change in the hybridisation of B and N atoms as a result of the following reaction :

$$BF_3 + NH_3 \longrightarrow F_3B.NH_3$$ (1)

4. Which of the two will have dipole moment ?

cis or trans – C_2H_2Cl (1)

5. How many σ and π bonds are present in naphthalene? (1)

6. Which out of NH_3 and NF_3 has higher dipole moment and why? (2)

7. Do ortho-nitrophenol and para-nitrophenol have hydrogen bonding in their molecules? Explain which of the two has higher boiling point?. (2)

8. Write M.O. electronic configuration of O_2 molecule. Compare its bond order with superoxide ion. (2)

9. Giving one example explain the shapes of following molecules :

(*i*) Molecule containing one lone pair and four bond pairs.

(*ii*) Molecule containing two lone pairs and three bond pairs.

(*iii*) Molecule containing two lone pairs and two bond pairs. (3)

10. Explain the following :

(*i*) Ionic compounds have high melting and boiling points.

(*ii*) Ice floats over water.

(*iii*) BeH_2 molecule has zero dipole moment although the Be—H bonds are polar. (3)

11. Discuss the shapes of following molecules using VSEPR model:

(*i*) $SiCl_4$ (*ii*) PH_3 (*iii*) $BeCl_2$

Which of these is/are polar molecules. (3)

12. (*a*) What is resonance? Write resonance structures of carbon dioxide molecule.

(*b*) Using the concept of hybridisation explain the shapes of

(*i*) C_2H_4 and (*ii*) C_2H_2 molecules.

(*c*) State the type of hybrid orbitals associated with

(*i*) P in PF_5 and (*ii*) S in SF_6 (5)

To check your performance, see HINTS and SOLUTIONS to some questions at the end of Part I of the book.

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UNIT 5

STATES OF MATTER : GASES AND LIQUIDS

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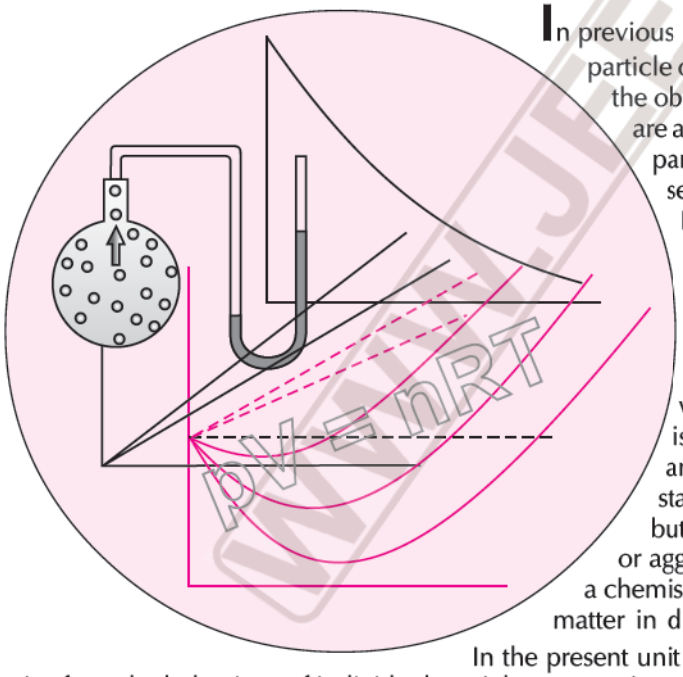

In previous units, we have learnt about the properties related to single particle of matter such as an atom or a molecule. However, most of the observable properties of a material are **bulk properties** which are associated with the collection of a large number of individual particles. These are very important because we can actually see these and help us to understand how the world works. For example, an individual molecule of a liquid does not boil but the bulk liquid boils. The individual water molecules do not wet but water which represents a collection of water molecules has wetting properties. We speak of different forms of water such as ice (the solid form of water) liquid water and steam (the gaseous form of water). In all the three states of water, chemical composition is same (*i.e.*, H_2O). But the physical properties of ice, water and steam are very different. The characteristics of three states of matter depend not only on the energies of molecules but also on the manner in which the individual particles bind or aggregate to form bulk materials. Therefore, it is necessary for a chemist to know the physical laws which govern the behaviour of matter in different states.

In the present unit we will learn about how the bulk properties of materials arise from the behaviour of individual particles; atoms, ions or molecules. We shall also learn more about the different physical states of matter particularly, gaseous and liquid states.

THREE STATES OF MATTER

Matter exists in three different physical states, namely *solid, liquid* and *gaseous* states. The important characteristics of three states are:

Solid state. *A solid possesses a definite size (volume) and a definite shape*. The shape of a solid can be changed but it usually requires considerable force. Therefore, solids are generally hard and rigid. Some common examples of solids are iron, silver, common salt, etc.

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Liquid state. *A liquid possesses a definite volume but not definite shape*. It takes up the shape of the container in which it is placed. Liquid also has a tendency to flow. For example, water, alcohol, milk, oil, etc.

Gaseous state. *A gas neither possesses a definite volume nor definite shape*. A gas occupies the whole of the volume of the vessel in which it is placed. It also takes up the shape of the container. For example, air, carbon dioxide, oxygen, hydrogen, etc.

However, it may be noted that a substance may exist in any of the three states under appropriate conditions of temperature and pressure. As we all know, water can exist in three states of matter as *ice* (solid), *water* (liquid) or *steam* (gas). In general, a substance is said to be :

- a **solid** if its melting point is above room temperature under atmospheric pressure;
- a **liquid** if its melting point is below room temperature and boiling point is above room temperature and
- a **gas** if its boiling point is below room temperature under atmospheric pressure.

It may be noted that a given substance may also exist simultaneously in all the three states under certain specific conditions of temperature and pressure. For example, water exists in all the three phases simultaneously *i.e.* ice, water and water vapour at 0.01°C and 4.58 mm of Hg pressure.

The temperature at which all the three phases of the same substance exist simultaneously is called **triple point.**

KEY NOTE

It may be noted that now scientists are talking about **five states of matter**. In addition to solid, liquid and gaseous state, there are two more states of matter known as plasma and Bose Einstein Condensate (BEC).

The **plasma** state consists of super energetic and super excited particles and exists at very high temperatures. Plasma is an ionized gas, the gas into which sufficient energy is provided to free electrons from atoms or molecules and to allow both species *i.e.*, ions and electrons to coexist. The fluorescent tubes and neon sign bulbs consist of plasma. The sun and the stars also glow because of the presence of plasma in them.

The fifth state is **Bose Einstein Condensate** which consists of supercooled solid in which the atoms lose their individual identity and condense to form a single super atom. For example, the BEC state is formed by cooling a gas of extremely low density (about one hundredth of the density of air) to super low temperature.

However, we shall be concentrating on three common states of matter (solid, liquid and gaseous) in the present unit.

To understand the behaviour of various states of matter, scientists had been trying to understand the constituents of matter. In the present unit, we shall explain some of the important general characteristics in terms of the elementary constituting particles (known as microscopic approach).

INTERMOLECULAR FORCES

The forces of attraction and repulsion between interacting particles (atoms or molecules) are called **intermolecular forces.** Such forces exist in all states of matter and are responsible for many structural features and physical properties of matter.

The intermolecular forces are weak forces. These are present even in case of non-polar molecules such as H_2, O_2, Cl_2, CH_4, etc., in the solid and liquid states. It has been observed that even non-polar substances such as hydrogen, chlorine, methane, etc. can be liquefied. We all know that noble gases are monoatomic and their atoms do not combine to form molecules because they have stable filled electronic configurations. But these gases can also be liquefied. This means that some forces must be operating in their liquid state. These forces, are however, very weak as indicated by their low melting and boiling points.

	He	Ne	Ar	Kr	Xe	Rn
m.p. (K)	—	24.5	83.7	115.7	161.1	202.2
b.p. (K)	4.2	27.2	87.3	121	165	211

The existence of weak attractive intermolecular forces was first proposed by the Dutch scientist Johannes van der Waals, who studied the effect of these molecular forces on the behaviour of real gases. In his honour, these forces are called **van der Waals forces.** Such forces come into existence due to the interplay of the positive and negative charges between the neighbouring atoms of non-polar molecules when they are very close to each other.

Intermolecular forces arise due to the following types of interactions :

(*i*) Dispersion forces or London forces

(*ii*) Dipole-dipole forces

(*iii*) Dipole-induced dipole forces

(*iv*) Hydrogen bonding.

These are discussed below :

1. Dispersion forces or London Forces

Atoms and non-polar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But the intermolecular forces may exist even in these non polar atoms such as noble gases or non-polar

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molecules such as O_2, N_2, H_2 etc. This is because the noble gases and non-polar molecules can be liquefied suggesting that there must be some intermolecular attraction. In other words, a dipole may develop momentarily even in such atoms or molecules.

In order to understand the origin of these forces, let us consider two noble gas atoms A and B very close to each other. Each atom is uncharged because its electronic charge cloud is symmetrically distributed around the nucleus [Fig. 1 (*a*)]. However, due to the motion of the electrons, we can imagine that for a fraction of time, the electronic charge distribution in one of the atoms say 'A' becomes unsymmetrical, *i.e.* charge cloud is more on one side than the other. During this a very short period, the unsymmetrical centres of positive and negative charges do not coincide. As a result of instantaneous distribution of electrons in the atom, there is a small temporary dipole known as **instantaneous dipole**. This instantaneous or transient dipole distorts the electron distribution in the neighbouring atom 'B' and induces dipole known as **instantaneous induced dipole** [Fig. 1 (*b*) and 1 (c)]. The temporary dipoles of atom 'A' and 'B' attract each other. These attractive forces are also called **instantaneous dipole and instantaneous induced dipole forces.** Similarly, temporary dipoles are induced in non–polar molecules also. These forces of attraction were first studied by the German physicist Fritz London and therefore, these are known as **London forces.** These are also called **dispersion forces.**

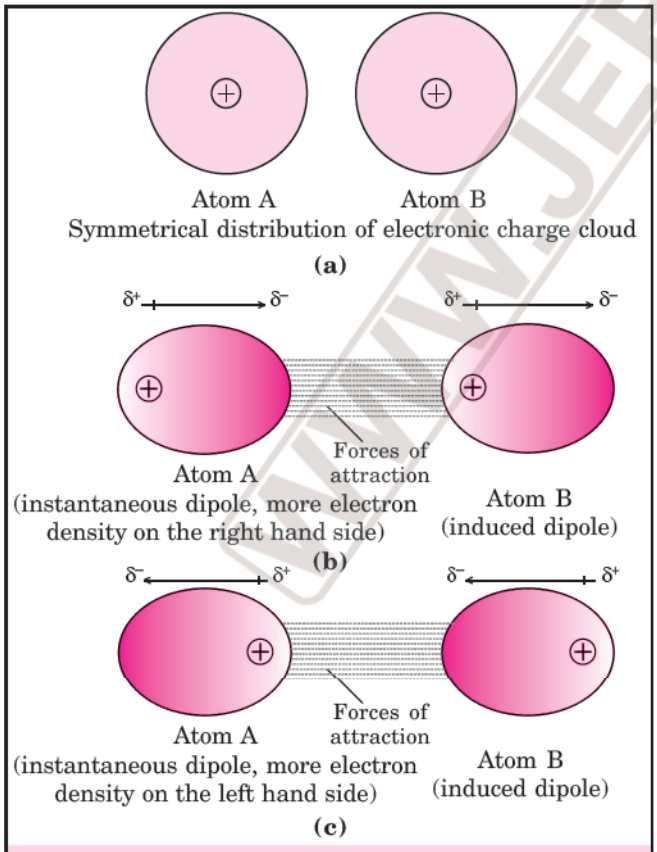

Fig. 1. Origin of instantaneous dipole-instantaneous induced dipole (Dispersion forces or London forces)

These forces are always attractive and the ***interaction energy due to these forces is proportional to the sixth power of the distance between two interacting particles (i.e., $1/r^6$ where r is the distance between two particles.*** These are significant only at short distances (about 500 pm). These also depend upon the polarizability of the atom or molecule.

The polarizability of an atom or a molecule is a measure of the ease with which the electrons and nuclei can be displaced from their average positions. The more easily the electrons and nuclei can be displaced, the greater is the polarizability. The larger the polarizability, the greater is the magnitude of instantaneous dipole and hence the stronger the London forces.

These forces are responsible for the condensation of noble gases and other gases such as H_2, Cl_2, CH_4, etc., which have no residual bonding capacity. In all such cases, the solids and liquids are formed through these interactions. However, these forces are very weak forces. The strength of the forces depends upon

(i) size of the molecule
(ii) number of electrons present in the molecule
(iii) molecular structure.

For example, large molecules have much diffused charged clouds. Hence, there are great chances of its distortion and producing instantaneous dipoles. Therefore, the strength of van der Waals' forces increases with molecular size. This is evident from the boiling points of methane (CH_4), silane (SiH_4) and germane (GeH_4) which increase from CH_4 (112 K) to SiH_4 (161 K) to GeH_4 (183 K) due to increase in molecular size.

Molecule	CH_4 Methane	SiH_4 Silane	GeH_4 Germane
Boiling point	112 K	161 K	183 K

Moreover, the larger the number of electrons in the molecules, the greater is the chances of distortion of electron clouds. For example, the boiling points of monoatomic noble gases increase from helium to radon.

The shape of the molecules also has a significant effect on the magnitude of London forces. For example, *n*-pentane, isopentane and neo-pentane have same molecular formula, C_5H_{12}. However, their boiling points are different. For example, the boiling point of *n*-pentane is about 27° higher than that of neo-pentane. The difference in boiling points is because of different shapes of the molecules; *n*-pentane has zig-zag chains, isopentane has one branch in the chain whereas neo-pentane has nearly spherical shape.

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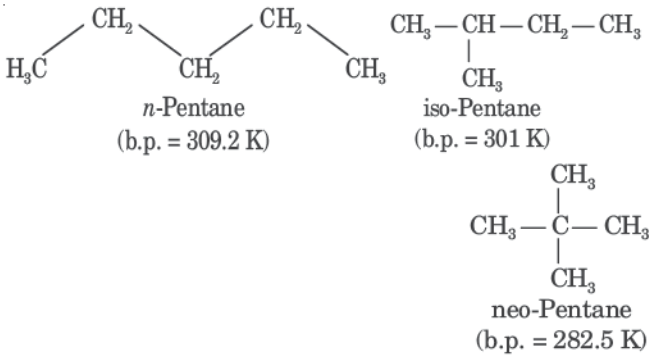

The branching of the chain makes the molecule more compact and thereby decreases the surface area. Therefore, the overall attraction between molecules which depend upon the surface area, becomes less and hence boiling point decreases with branching.

2. Dipole-dipole (or Keesom) forces :

These types of forces occur in molecules which have permanent electric dipole such as HCl, NH_3, H_2O, etc. A polar molecule has separate centres of positive and negative charges and the ends of the diploes possess "partial charges". These charges are shown by Greek letter *delta* (δ). The partial charges are always less than the unit electronic charge (1.6×10^{-19}C). These forces arise due to interactions between oppositely charged ends of the polar molecules. The positive end of one molecule attracts the negative end of the other molecule and vice versa. For example, the dipole-dipole interactions between the hydrogen chloride molecules are shown in Fig. 2.

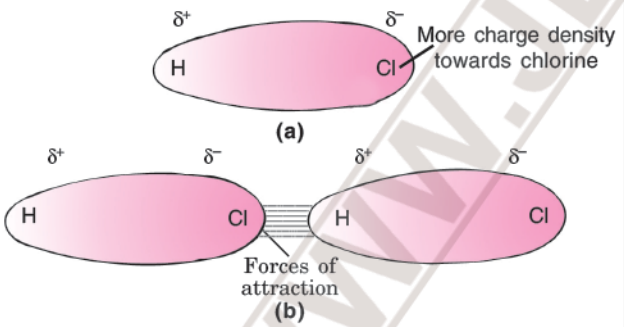

Fig. 2. (a) Distribution of electron cloud in polar HCl molecule. **(b)** Dipole-dipole interactions between two HCl molecules.

Greater the dipole moment of the molecules, greater are the forces of attraction. This effect was first studied by Keesom in 1912 and is also referred to as **orientation effect.** These forces are also called **Keesom forces** and produce a net attractive influence.

These interactions are stronger than London forces. However, these are weaker than ion-ion interactions because only partial charges are involved. The interactions decrease with the increase of distance between the dipoles. As in London forces, the interaction energy is inversely proportional to distance between polar molecules, ***Dipole–dipole interaction energy between stationary polar molecules (as in solids) is proportional to $1/r^3$ and that between rotating polar molecules is proportional to $1/r^6$,* where *r* is the distance between polar molecules.** The dipole-dipole interactions in a molecular solid are shown in Fig. 3.

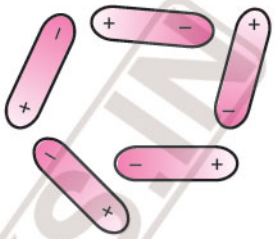

Fig. 3. Dipole-dipole forces in molecular solids.

It may be noted that besides dipole-dipole interactions, polar molecules can interact by London forces also. As a result, the cumulative effect is that the total intermolecular forces in polar molecules increase.

3. Dipole-induced dipole forces

These type of attractive forces operate between the polar molecule having permanent dipole and the molecules having no permanent dipole. For example, if the molecules of a substance are non-polar (such as noble gas, iodine molecule, etc.), they do not possess any dipole. However, when these molecules come into the neighbourhood of other molecules which have permanent dipole, an induced dipole appears on these non-polar molecules.

This is because the electron cloud of the non-polar atom or molecule gets deformed due to the electric field of the polar molecule. This causes a shift in the centre of gravity of the negative charge relative to the nuclear charge and results in the formation of an induced dipole moment. As the size of the atom or molecule increases, the influence of the electric dipole on it also increases.

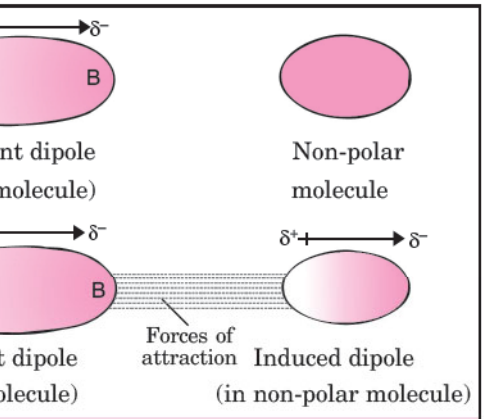

Fig. 4. Dipole-induced dipole interactions between permanent dipole and induced dipole.

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The interaction energy is also proportional to $\frac{1}{r^6}$ ***and depends upon the dipole moment of the polar molecule and polarizability of the non-polar atom or molecule.*** Molecules or atoms of larger size have more tendency to get polarized.

The forces existing between dipole and induced dipole are called **dipole-induced dipole forces.** The easier the molecules are deformed (easily polarizable), the greater are the attractive forces. This effect was studied by Debye in 1920 and is known as **induction effect.**

In this case also, comulative effect of dispersion forces and dipole-induced dipole interactions exist.

The above three types of forces are collectively known as **van der Waals forces.** The magnitude of each type of interaction will vary depending upon the type of molecules.

4. Hydrogen bond

Hydrogen bond is a special case of **dipole-dipole interactions.** When hydrogen atom is bonded to atoms of highly electronegative elements such as fluorine, oxygen or nitrogen, the hydrogen atom forms a weak bond with the electronegative atom of the other molecule. This weak bond is called **hydrogen bond.** For example, in hydrogen fluoride, HF, hydrogen atom forms a weak bond with fluorine atom of the neighbouring molecule, while remaining bonded to its fluorine atom. This may be shown as :

$$\overset{\delta+}{H}\text{——}\overset{\delta-}{F}\cdots\cdots\overset{\delta+}{H}\text{——}\overset{\delta-}{F}\cdots\cdots\overset{\delta+}{H}\text{——}\overset{\delta-}{F}\cdots\cdots$$

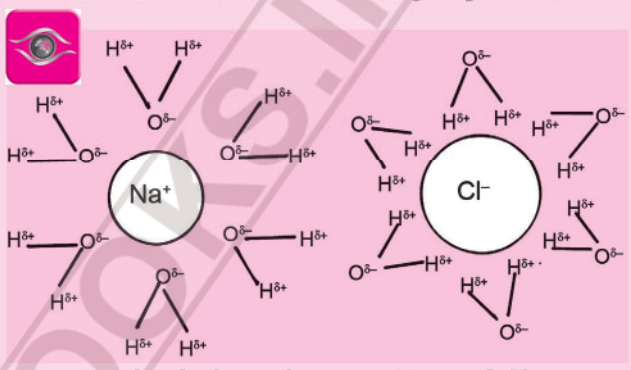
In other words, hydrogen (atom acts as a bridge) between two atoms, holding one atom by a covalent bond and the other atom by a hydrogen bond. The hydrogen bond is represented by dotted line (....) while the covalent bond is represented by solid line (—). As a result of hydrogen bonding, HF exists as a cluster of hydrogen fluoride molecules and is represented as $(HF)_n$. It may be noted that although hydrogen bonding is regarded as being limited to N, O and F but some molecules containing Cl may also participate in hydrogen bonding.

The energy of hydrogen bond varies between 10 to 100 kJ mol^{-1}. This is quite a significant amount of energy and therefore, hydrogen bonds are powerful force in determining the properties of many compounds. These play significant role in proteins and nucleic acids. The strength of hydrogen bond is determined by the coulombic interactions between the lone pair of electrons of the electronegative atom of one molecule and hydrogen atom of the other molecule.

KEY NOTE

Ion-Dipole Interactions

We also come across attractive forces between an ion and dipole known as **ion-dipole forces.** Ion-dipole interactions are between an ion (either a cation or an anion) and a polar molecule. The strength of these forces depends on the charge and size of the ion and on the magnitude of the dipole moment and size of the polar molecule. The charge density on cations is more than on anions and therefore, a cation interacts more strongly with dipoles than anion having same charge but bigger size. The common example of ion-dipole interaction is the hydration of ions. For example, when sodium chloride is dissolved in water, it gets split up into Na^+ and Cl^- ions. These ions get surrounded by water molecules which have a large dipole moment.



Ion-dipole forces between Na^+ and Cl^- ions and water molecules.

Due to hydration of the ions, the water molecules act as a dielectric to keep the ions separated and therefore, NaCl dissolves in water. On the other hand, carbon tetrachloride (CCl_4) is non-polar and its molecules cannot have ion-dipole interactions. Therefore, NaCl does not dissolve in CCl_4 and CCl_4 acts as a poor solvent for ionic compounds.

It may be noted that **ion-dipole forces are not van der Waals forces.** The term **van der Waals forces** refers only to dipole-dipole, dipole-induced dipole and dispersion forces.

Intermolecular forces discussed so far are all attractive forces. However, **molecules also exert repulsive forces on one another.** When two molecules are brought into close contact with each other, the repulsion forces may also start operating. These are between the electron clouds and between the nuclei of two molecules. The magnitude of repulsive forces increases rapidly as the distance between the molecules decreases. This is the reason that liquids and solids are hard to compress. In liquids and solids, the molecules are already close and therefore, they resist further compression because that would result in the increase of repulsive interactions.

THERMAL ENERGY

The *thermal energy* is the ***energy of a body due to motion or movement of its atoms or molecules.***

It is directly proportional to the temperature of the substance. It is a measure of average kinetic energy of the particles of the matter and is therefore, responsible for the movement of particles. This movement of the particles, therefore, is also called **thermal motion** and keeps the molecules apart.

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INTERMOLECULAR FORCES VERSUS THERMAL ENERGY OF THREE STATES OF MATTER

A substance may exist in any of the three states of matter (i.e., solid, liquid or gas) depending upon the conditions of temperature and pressure. According to **particle concept of matter,** all matter consists of tiny particles (atoms or molecules) which are constantly moving in all directions. These particles exert attractive forces upon one another called **inter-particle** (or **intermolecular) forces**. These inter-particle forces are quite stronger in solids than those in liquids and are very small (negligible) in gases.

The three states of matter arise due to the competition between **molecular interaction energy** which keeps molecules together and the **thermal energy** which moves the molecules apart. ***The competition between molecular interaction energy and thermal energy determines whether a given substance under given conditions is a gas, a liquid or a solid.***

In **gases,** the molecules have weakest (almost negligible) molecular interactions (i.e., no attractive forces) but highest thermal energy. Therefore, the molecules in gases can move at random in all directions with high speeds.

In **solids,** the molecular interactions are strongest but the thermal energy is weakest and therefore, the molecules in solids have no translatory motion and can only oscillate with respect to their equilibrium positions. Therefore, the solids can have only vibratory motion.

In **liquids**, the two types of energies are intermediate between solids and gases.

Some of the properties of solids, liquids and gases can be explained on the basis of intermolecular forces and thermal energy. As we have learnt, the intermolecular forces tend to keep the molecules together while thermal energy of the molecules tends to keep them apart.

- In solids, the net forces between the molecules are attractive forces. When the molecules are forced to come very close, the forces become repulsive. Moreover, the molecules in the solid with relatively low thermal motion cannot overcome the attractive forces and cannot move independently. However, on ***heating, the thermal motion increases and the solid melts***.
- In liquid state, there is a balance between attractive intermolecular forces and thermal motion. The molecules can have translatory motion but cannot become completely free like gases. In solids and liquids, molecules cannot be pushed together by external pressure because the intermolecular forces become repulsive at small distances between the molecules. Therefore, ***the solids and liquids cannot be easily compressed***. Therefore, only small changes in volume occur on their interconversion from solid to liquid and vice-versa.

The breaking and making of bonds between molecules in liquid gives it a non-rigid structure. This explains as to why ***liquids do not have any definite shape although they have definite attractive interaction energy*** between the molecules.

- In gases, there are large empty spaces between the molecules and these can be readily compressed when pressure is applied. Hence, ***the gases are highly compressible*** unlike solids and liquids.

In gases, the intermolecular forces are very weak and molecules donot cling together to make liquid or solid unless thermal energy is reduced by lowering the temperature. Therefore, ***the gases donot liquify on compression only***. However, when thermal energy of molecules is reduced by lowering the temperature, the gases can be very easily liquified.

Thus, we may conclude that *the predominance of molecular interactions results into change of gases to liquid to solid state while predominance of thermal energy results into change of solid to liquid to gas* as shown below :

Molecular interaction energy

GAS ⟶ LIQUID ⟶ SOLID

Predominance of intermolecular interactions

Thermal energy

GAS ⟵ LIQUID ⟵ SOLID

Predominance of thermal energy

TYPE OF BONDING AND MELTING AND BOILING POINTS

We have learnt about the role of intermolecular forces and thermal energy in determining a particular state of matter. These three states of matter are inter-convertible by changing the conditions of temperature and pressure. For example, water is a liquid at ordinary temperature. It can be changed into steam (gas) by heating at 100°C whereas, it can also be changed into ice (solid) by cooling below 0°C.

$$\underset{\text{(Solid)}}{\text{Ice}} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \underset{\text{(Liquid)}}{\text{Water}} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \underset{\text{(Gas)}}{\text{Steam}}$$

When a solid is heated, it melts to form a liquid. *The temperature at which a solid melts to become a liquid* is called its ***melting point.***

On further heating, a liquid changes to vapour. *The temperature at which a liquid changes to vapour* is known as its **boiling point.**

The intermolecular forces of attraction between the particles constituting the matter (atoms, ions or molecules) influence the temperature at which the substance melts or boils. If the intermolecular forces of attraction are strong, the melting point and boiling

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point will be high and if these forces are weak, the melting point and boiling point will be low. For example, we expect to have low melting and boiling points of noble gases because only the weak London dispersion forces hold the atoms together in the solid or liquid states.

Simple covalent molecules such as H_2, F_2, O_2, CH_4 etc. are gases at room temperature. They form molecular crystals which have low melting and boiling points. The intermolecular interactions between these covalent molecules are only weak London dispersion forces. Therefore, they have low melting and boiling points.

The polar molecules generally have higher boiling points than non-polar molecules of similar mass because of the dipole-dipole forces of attraction between polar molecules.

It may be noted that in case of **ionic substances,** exceedingly high temperatures are required to melt or boil these substances because of strong interionic forces. Similarly, the forces holding the atoms together in metals are very strong. Therefore, metals in general, have very high melting and boiling points.

GASEOUS STATE OF MATTER

Gaseous state is the simplest state of matter. A look at the periodic table shows that only **eleven** elements are gases under normal conditions as shown in Fig. 5.

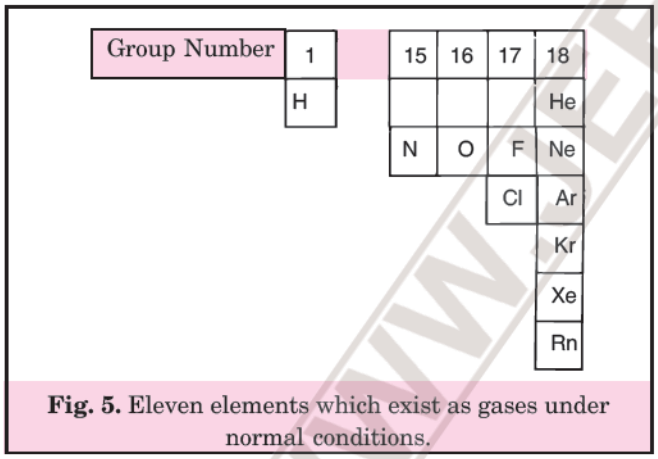

Fig. 5. Eleven elements which exist as gases under normal conditions.

General Characteristics of Gases

The gaseous state is characterized by the following physical properties.

1. Shape and volume : Gases neither has definite shape nor definite volume. They assume volume and shape of the container.

2. Compressibility : Gases can be compressed by the application of external pressure.

3. Homogeneous nature : Gases have similar composition in all parts and are therefore, homogeneous in nature.

4. Density : Gases have much lower density than the solids and liquids.

5. Pressure : Gases exert pressure equally in all directions.

6. Liquefication : Gases can be liquefied by cooling and by applying pressure.

7. Diffusion : Gases intermix readily and completely in all proportions without any mechanical aid.

R U Curious...

- **CO_2 is heavier than N_2 and O_2 gases present in the atmosphere. But it does not form the lower layer of the atmosphere.**
  - Gases possess the property of diffusion which is independent of the force of gravitation. Due to diffusion, gases mix with each other and remain almost uniformly distributed in the atmosphere.

MEASURABLE PROPERTIES OF GASES

The important measurable properties of gases are *mass (amount), volume, pressure, temperature, viscosity and specific heat.*

These are discussed below:

1. Measurement of Mass

The mass or amount of a gas can be measured by weighing. The container in which the gas is enclosed is first weighed. Then the weight of the container after removing all the gas is again measured. The difference between the two weights gives the mass of the gas. That is,

$$\text{Mass of gas} = \begin{bmatrix}\text{Weight of container}\\ \text{containing the gas}\end{bmatrix} - \begin{bmatrix}\text{Weight of container after}\\ \text{removing all the gas}\end{bmatrix}$$

Units of mass. In SI units, mass is generally expressed in kilograms (*kg*). Quite often, it is also expressed in grams ($1\ kg = 10^3\ g$).

The mass (or amount) of gas (m) is commonly expressed in terms of number of moles (n). The mass is related to the number of moles as

$$n\ (\text{number of moles}) = \frac{m(\text{mass in grams})}{\text{M(molar mass)}}$$

where M is molar mass.

2. Measurement of Volume

The volume of a substance is the *space occupied by it*. Since a gas occupies the entire space of the container available to it, the volume of a gas is the same as the volume of the container. Therefore, the measurement of the volume of a gas only requires the measurement of the volume of the container enclosing it.

Units of volume. Generally, the volume is expressed in units of litres (L), millilitres (ml) or cubic centimetres (cm^3). The different units are related as

$$1\ ml = 1\ cm^3$$
$$1\ L = 10^3\ cm^3 \text{ or } = 1\ dm^3 \text{ or } = 10^{-3}\ m^3$$

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In the S.I. units, volume is measured in cubic metre (m^3). However, this unit is not commonly used because it is too large. Volume is generally expressed in units of dm^3 or cm^3. The conversion factors are :

$$1\ m^3 = 10^3\ dm^3 = 10^6\ cm^3$$

3. Measurement of Pressure

Pressure is force per unit area. Gases exert uniform pressure in all the directions on the walls of the container in which they are confined. Thus, *the* **pressure** *of the gas is the force exerted by the gas per unit area of the walls of the container.*

Atmospheric Pressure

The earth is surrounded by an approximately 800 km thick blanket of air. The air is pulled towards the surface by gravity and therefore, it exerts pressure on earth's surface. *The pressure exerted by the gases of the atmosphere on the surface of the earth* is called **atmospheric pressure.**

Measurement of Atmospheric Pressure

It is measured by an instrument known as barometer. A simple barometer can be constructed by taking a glass tube (approximately 80 cm long) closed at one end and filling it with pure mercury. The tube is then carefully inverted into an open vessel of mercury as shown in Fig. 6. The mercury level in the tube drops until the pressure due to the column of mercury in the tube becomes equal to the atmospheric pressure acting outside the tube. *This is the reason that whole of the mercury does not run out.* The region above the mercury in the tube is almost perfect, vacuum, therefore, the pressure due to mercury column is equal to atmospheric pressure.

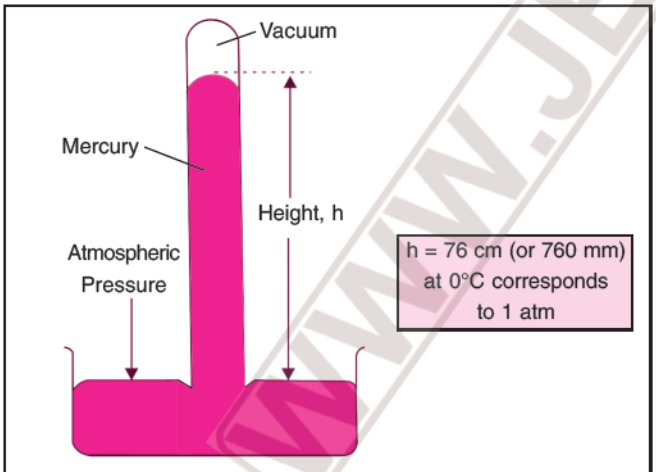

Fig. 6. A mercury barometer.

Thus, the height of the mercury column gives the atmospheric pressure. When the pressure of the atmosphere decreases, the height of the column decreases. On the other hand, when the atmospheric pressure increases, the height of the mercury increases. The pressure of the atmosphere is not constant but changes from place to place and time to time.

R U Curious...

❑ **Mercury is used as a liquid in barometers.**

▶ Mercury is generally used as a liquid in barometers because of the following reasons:

(*i*) The height of the column in a barometer is inversely proportional to the density of the liquid, *i.e.* less dense the liquid higher will be the column. Since mercury is very dense, it is best for barometers because it supports column of convenient height.

(*ii*) Mercury is not volatile at ordinary temperatures and therefore, the pressure exerted by the vapours above the mercury column is very small and can be neglected.

Units of atmospheric pressure

The maximum height of mercury which can be supported by the atmospheric pressure provides a measure of that pressure. The pressure expressed in terms of height of mercury column can be converted into the units of force per unit area. Let a mercury height of h cm and area of cross-section 'a' cm^2 exert a downward force equal to the weight of the mercury column. The force per unit area of surface is P so that

$$P = \frac{\text{Force}}{\text{Area}}$$

But $\quad \text{Force} = \text{Mass} \times \text{Acceleration}$

$$\therefore \quad P = \frac{\text{Mass} \times \text{Acceleration}}{\text{Area}} = \frac{mg}{A}$$

where m is the mass of the mercury in the tube and g is the acceleration due to gravity. If d is the density of the mercury, the mass is given by

$$m = d \times V$$

where V is the volume of the mercury in the tube.

Substituting the value of m in the expression for P, we get

$$P = \frac{d \times V \times g}{A}$$

But $\quad \text{Volume, } V = \text{Area} \times \text{Height} = a \times h$

$$\therefore \quad P = \frac{d \times A \times h \times g}{A}$$

$$= hdg$$

By international agreement, **a standard pressure of one atmosphere (1 atm) is defined as the pressure that will support a column of mercury of 76 cm height at 0°C** (density of mercury = 13.5951 g cm^{-3}) and at standard gravity = 980.665 cm s^{-2}. One atmosphere is also referred to as 760 torr. This unit is named after the name of Italian scientist Torricelli, who invented the barometer. Thus,

1 atm = 76.0 cm of mercury (cm Hg)
= 760 mm of mercury (mm Hg)
= 760 torr.

The SI unit of pressure is **pascal (Pa)**. It is defined as *the pressure exerted when a force of 1 newton (1 N) acts on a 1m^2 area.*

$$1\ Pa = 1\ Nm^{-2} = 1\ kg\ m^{-1}\ s^{-2}$$

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For gases, this unit is too small and generally we express the pressure of the gas in terms of **bar** and we have

$$1 \text{ bar} = 100 \text{ kPa or} = 10^5 \text{ Pa}$$

Pascal and bar are also related to atmosphere as :

1 atm = 1.01325 bar = 1.01325 × 10^5 Pa = 101.325 kPa

or **1 bar = 0.987 atm**

It may be noted that for approximate work, one atmosphere may be taken to be equal to 10^2 kPa or 10^5 Pa or Nm^{-2}.

Measurement of Pressure of Gas

The pressure of gases are measured by a device known as **manometer.** There are two types of manometers in common use. These are :

(*i*) *Open end manometer and*

(*ii*) *Closed end manometer.*

(*i*) **Open end manometer.** It consists of a U-shaped tube with one limb shorter than the other. It is partially filled with mercury. The shorter limb is connected to the vessel containing the gas whereas, the longer limb is open as shown in Fig. 7.

The mercury in the longer limb is subjected to the atmospheric pressure while the mercury in the shorter limb is subjected to the pressure of the gas.

The difference in the levels of the mercury in the two limbs gives the difference of pressure on the two sides. That is,

Atmospheric pressure – Gas pressure = Difference in the mercury levels in the two columns.

∴ Gas pressure = Atmospheric pressure – Difference in the mercury levels in the two columns.

i.e. $$p_{gas} = p_{atm} - h$$

where *h* corresponds to the difference in the levels of mercury in the two limbs.

For example, as given in Fig. 7 (*a*), the difference in the mercury levels in the two limbs is equal to 250 mm Hg, whereas the atmospheric pressure is 750 mm Hg. Therefore,

$$\text{Gas pressure} = 750 - 250 = 500 \text{ mm Hg}$$

It may be noted that if the mercury level in the open end tube is more than the other, this means that the pressure of the gas is more than that of the atmosphere. Obviously,

Pressure of gas = Atmospheric pressure + Difference in mercury levels in two columns.

$$p_{gas} = p_{atm} + h$$

(*ii*) **Closed end manometer.** It also consists of a U-shaped tube with one limb shorter than the other. It is partially filled with mercury. The shorter limb is to be connected to the vessel containing the gas whose pressure is to be determined whereas the longer limb is closed as shown in Fig. 7 (*b*). The space above the mercury on the closed end side is completely evacuated. The gas will exert a force on the mercury and thereby force the level down in the near side and up in the far side of the manometer. This give rise to a difference in mercury levels in the two limbs which is equal to the pressure of the gas. Thus

P_{gas} = Difference in mercury levels in the two limbs.

For example, as shown in Fig. 7 (*b*), the difference in mercury levels in the two limbs is 350 mm Hg. Therefore,

Pressure of the gas = 350 mm Hg

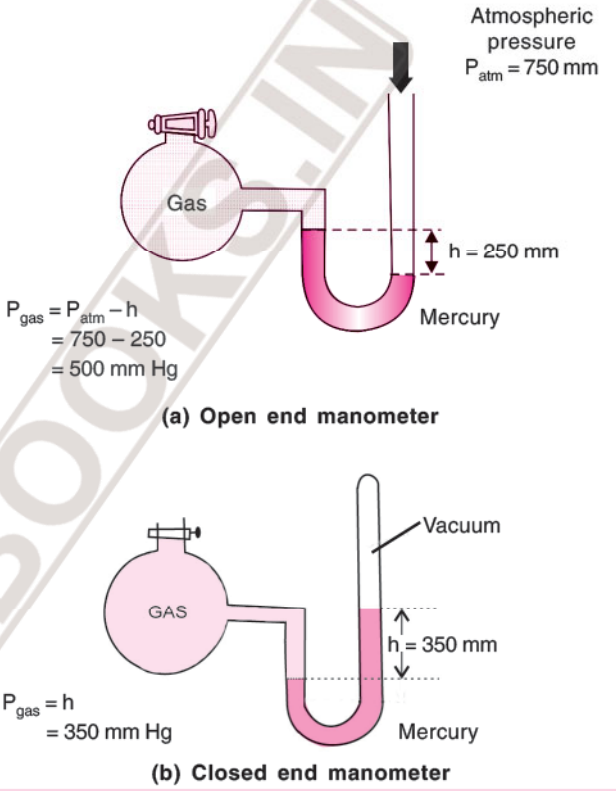

Fig. 7. (*a*) Open end manometer (*b*) Closed end manometer.

It may be noted that pressure is obtained in pascal when *h*, *d* and *g* are expressed in SI units.

4. Measurement of Temperature

Temperature *is a measure of hotness or coldness of a body.* The hot body is said to be at a higher temperature and the cold body is said to be at a lower temperature.

The measurement of temperature is based on the fact that many substances expand on increasing the temperature. The devices used to measure the temperature are called *thermometers.* The substance most commonly used in the thermometers is mercury.

Scales of temperature*

There are several temperature scales in common use. The most important of these is *Celsius scale* (previously known as centigrade scale).

* The temperature may also be expressed in **Fahrenheit scale,** after the name of a German instrument maker, Daniel Fahrenheit. This scale is based on taking freezing point of water as 32°F and boiling point of water as 214°F and dividing the range into 180 equal parts. The conversion method is $°C = \frac{5}{9}(°F - 32)$ or $°F = \frac{9}{5}(°C) + 32$.

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The S.I. unit of temperature is degrees Kelvin (K) and the scale is known as *Kelvin scale*. The zero point on the Kelvin scale is known as absolute zero which is equal to –273.15°C.

The temperature on the Celsius scale is converted to temperature on Kelvin scale by the addition of 273.15°. Thus,

$$°C + 273.15 = K$$

It may be noted that for simplicity 273.15 is commonly expressed as 273 in almost all calculations.

Standard Temperature and Pressure

The properties of a gas depend upon the temperature and pressure. Hence, it is convenient to specify a particular temperature and pressure for comparison of different gases. The standard conditions of temperature and pressure are abbreviated as S.T.P. or N.T.P. meaning *standard temperature and pressure or normal temperature and pressure* respectively. These are :

Standard temperature and pressure (S.T.P. or N.T.P.)

Temperature = 0°C or 273.15 K

Pressure = 1 atm or 760 mm Hg or 760 torr or 101.325 kPa (SI units) or 1 bar

Thus, STP denotes 0°C (or 273.15 K) temperature and 1 atm (101.325 kPa) pressure. However, a term **Standard ambient temperature and pressure (SATP)** is also used in some scientific works. SATP conditions means 298.15 K and 1 bar (*i.e.,* exactly 10^5 Pa).

GAS LAWS

We know that the volume of a gas depends upon the amount of gas, pressure and temperature. From the study of the behaviour of gases, certain generalisations were made. These generalisations are called **gas laws.** These gas laws give quantitative relationships between any two variables when the other two are kept constant. Let us discuss the various gas laws in detail.

1. Boyle's Law (Pressure-Volume Relationship)

In 1662, Robert Boyle studied the changes in volume of a gas by varying pressure at a constant temperature of a fixed amount of gas. He used a 'J' shaped glass tube as shown in Fig. 8. He trapped some air in the tip of the tube and measured the pressure exerted by the gas by noting the difference in height of the mercury in two arms of the tube (h). The pressure of the gas is increased by adding more mercury to the tube and volume of the gas becomes smaller. In this way, Boyle studied the relationship between the pressure and volume of a given mass of a gas at constant temperature.

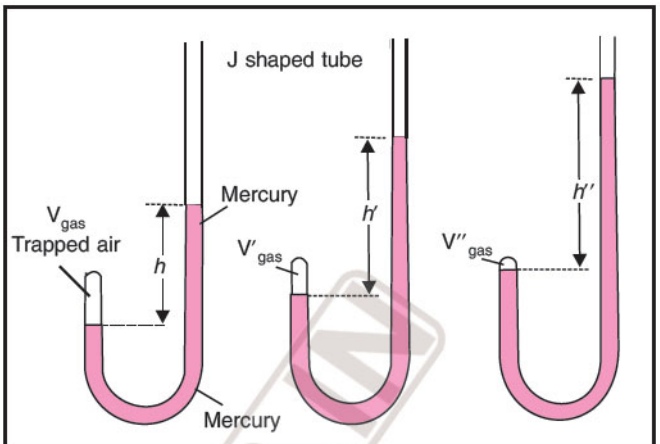

Fig. 8. Boyle's apparatus for studying relationship between pressure and volume at constant temperature.

The relationship is known as **Boyle's law.** It states that

at constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure.

Mathematically, Boyle's law may be expressed as :

$$V \propto \frac{1}{p} \quad (n, T \text{ constant})$$

i.e. $$V = \frac{k_1}{p}$$

where V is the volume, p is the pressure of the gas and k_1 is a constant of proportionality whose value depends upon the amount of the gas and temperature. The value of k_1 also depends upon the units in which p and V are expressed.

On rearrangement, we can write

$$pV = k_1 = \text{constant (at constant } n \text{ and T)}$$

It means that at **constant temperature, product of pressure and volume of a fixed amount of gas is constant.**

Let V_1 be the volume of a given mass of gas at pressure p_1 and at a given temperature T. When the pressure is changed to p_2 at the same temperature, let the volume changes to V_2. According to Boyle's law,

$$p_1V_1 = p_2V_2 = \text{constant (at constant temperature)}$$

or $$\frac{p_1}{p_2} = \frac{V_2}{V_1}$$

Hence, the Boyle's law may also be stated as the

product of pressure and volume of a given mass of a gas at constant temperature is constant.

This means that if the volume of the gas is doubled, the pressure will be reduced to one-half of its initial value and if volume is tripled, the pressure is lowered to one-third. Similarly, if pressure is made four times, the volume is reduced to 1/4 and so on.

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Experimental verification of the law

Boyle's law can be verified by measuring the volume for a given mass of gas at different pressures keeping the temperature constant. The experimental pressure-volume data for 0.09 mol of CO_2 gas at 300 K are given in Table 1. It is obvious that with the increase in pressure, the volume decreases and the value of pV remains practically constant. This demonstrates the validity of Boyle's law.

Table 1. Pressure-volume data for 0.09 mol of CO_2 at 300 K.

Pressure (p) (10^4 Pa)	Volume (V) ($10^{-3}m^3$)	Pressure × Volume (pV) (10^2 Pa m^3)
2.0	112.0	22.40
2.5	89.2	22.30
3.5	64.2	22.47
4.0	56.3	22.50
6.0	37.4	22.44
8.0	28.1	22.48
10.0	22.4	22.40

Graphical representation of the law

Boyle's law can also be illustrated by means of pressure-volume curves as shown in Fig. 9 to 12. When the pressure of the gas (p) is plotted against volume (V), by keeping (V) along x-axis and (p) along y-axis, we get a curve as shown in Fig. 9. The curve clearly shows that when volume is increased, pressure decreases and *vice versa*. At a particular state corresponding to volume V_1, pressure is p_1 and when volume is increased to V_2, the corresponding p_2 is smaller than p_1. Similar curves are shown at other temperatures (Fig. 10). Higher curves correspond to higher temperature.

Alternatively, if the graph is plotted between p and 1/V, a straight line passing through origin is obtained as shown in Fig 11. It means that at constant temperature, product of pressure and volume of a fixed amount of gas is constant. The plots of p versus 1/V obtained at different temperatures are shown in Fig. 11.

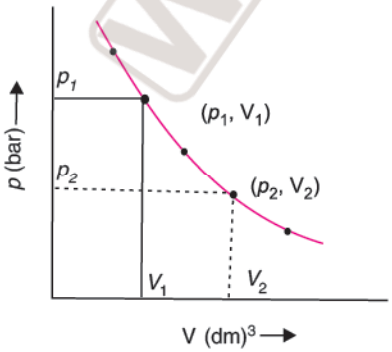

Fig. 9. Variation of p and V at constant T.

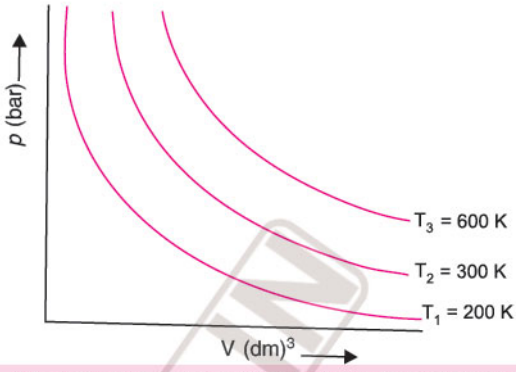

Fig. 10. Plots of p versus V at different temperatures.

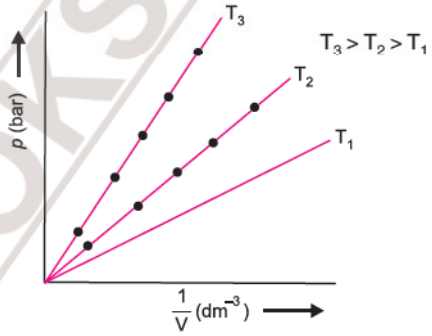

Fig. 11. Plots of p versus 1/V at different temperatures.

However, if the graph is plotted between the product pV along y-axis and pressure p along x-axis, we get the horizontal line (Fig. 12). This indicates that pV remains constant even if we change the pressure. The curve changes with change in temperature and separate curves are shown for each fixed temperature. ***The curves obtained by plotting (pV) against pressure (p) at different temperatures*** *are known as* **isotherms** (Fig. 12).

The higher curve corresponds to higher temperature.

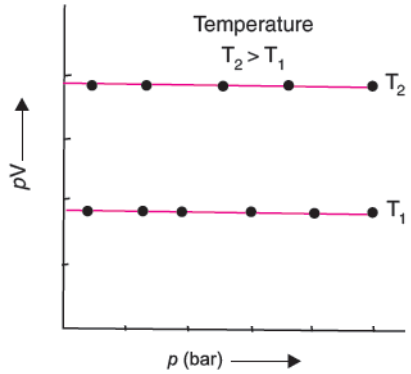

Fig. 12. Variation of pV with p.

It may be noted that Boyle's law is obeyed only by a hypothetical gas called **ideal gas.** However, gases like nitrogen, oxygen, carbon dioxide, etc. obey Boyle's law at low pressures and high temperatures and behave

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as ideal gases. At higher pressures and low temperatures, these gases donot obey Boyle's law.

We know that density is mass per unit volume so that

$$d = \frac{m}{V}$$

If we put the value of V in this equation, from Boyle's law equation, we obtain the relation as :

$$d = m\frac{p}{k_1} \text{ or } = \left(\frac{m}{k_1}\right) p = k' p$$

This shows that at *a constant temperature, pressure is directly proportional to the density of a fixed mass of the gas.*

Practical significance of Boyle's law.

The Boyle's law proves a very important fact that the **gases are highly compressible**. When a given mass of gas is compressed by increasing the pressure, the same number of molecules occupy a smaller space. As a result, the gas becomes denser because mass per unit volume increases. For example, air at sea level is dense, but the density as well as the pressure decrease with increase in altitude. For example, the atmospheric pressure at Mount Everest is only about 0.5 atm. As a result, the oxygen in air becomes insufficient for normal breathing. This causes what is commonly known as **altitude sickness** (general uneasiness, sluggish feeling, headache, etc.). Therefore, mountain climbers and the *jawans* in altitudes like Ladakh, undergo extensive training to adapt their bodies to low oxygen pressure or they carry oxygen cylinders for an emergency.

Similarly, interiors of jet aeroplanes which fly at very high altitudes (about 10,000 m) are artificially maintained at normal pressure to have proper oxygen for breathing. They are also equipped with emergency oxygen supply in case of pressure falls.

R U Curious...

❑ **While pumping air into a cycle tyre, a boy noticed that volume as well as pressure is increasing. Does Boyle's law fail here!**

▶ The law is applicable only for a fixed mass of gas. As the boy fills air into the cycle tyre, he is adding more and more air into the tyre. Hence, he is increasing the mass of air inside the tyre and therefore, the law is not applicable.

SOLVED EXAMPLES

❑ **Example 1.**

A gas occupies 200 mL at a pressure of 0.820 bar at 20°C. How much volume will it occupy when it is subjected to external pressure of 1.025 bar at the same temperature ?

Solution: $p_1 = 0.820$ bar $\quad p_2 = 1.025$ bar

$V_1 = 200\ ml \quad V_2 = ?$

Since temperature is constant, therefore, by applying Boyle's law,

$$p_1V_1 = p_2V_2 \quad \text{or} \quad V_2 = \frac{p_1V_1}{p_2}$$

$$V_2 = \frac{(0.820 \text{ bar}) \times (200 \text{ mL})}{1.025 \text{ bar}} = \mathbf{160\ ml}$$

❑ **Example 2.**

A vessel of 120 mL capacity contains a certain amount of gas at 35°C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35°C. What would be its pressure ?

N.C.E.R.T.

Solution: Since temperature and amount of gas remains constant, therefore, Boyle's law is applicable.

$p_1V_1 = p_2V_2$

$p_1 = 1.2$ bar $\quad p_2 = ?$

$V_1 = 120$ mL $\quad V_2 = 180$ mL

$\therefore\ 1.2 \times 120 = p_2 \times 180$

$$\therefore \quad p_2 = \frac{1.2 \times 120}{180} = 0.8 \text{ bar}$$

❑ **Example 3.**

A gas occupies a volume of 250 mL at 745 mm Hg and 25°C. What additional pressure is required to reduce the gas volume to 200 mL at the same temperature ?

Solution: $p_1 = 745$ mm Hg $\quad p_2 = ?$

$V_1 = 250$ mL $\quad V_2 = 200$ mL

Since temperature remains constant, therefore, by applying Boyle's law,

$p_1V_1 = p_2V_2$

$$\text{or} \quad p_2 = \frac{p_1V_1}{V_2} = \frac{(745 \text{ mm Hg}) \times (250 \text{ mL})}{(200 \text{ mL})}$$

$= 931.25$ mm Hg

The additional pressure required = 931.25 – 745 = **186.25 mm.**

❑ **Example 4.**

A balloon is filled with hydrogen at room temperature. It will burst if pressure exceeds 0.2 bar. If at 1 bar pressure the gas occupies 2.27 L volume, upto what volume can the balloon be expanded ?

N.C.E.R.T.

Solution: According to Boyle's law, at constant temperature,

$p_1V_1 = p_2V_2$

If $p_1 = 1$ bar then $V_1 = 2.27$ L

If $p_2 = 0.2$ bar, then

$$V_2 = \frac{p_1V_1}{p_2}$$

$$= \frac{1 \text{ bar} \times 2.27 \text{ L}}{0.2 \text{ bar}}$$

$$= \mathbf{11.35\ L}$$

Since balloon bursts at 0.2 bar pressure, the volume of the balloon should be less than 11.35 L.

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Practice Problems

1. 5 L of air at 750 mm mercury pressure were compressed into an iron cylinder of 1 L capacity. What will be the new pressure in atmosphere if the temperature remains constant ?

2. A weather balloon has a volume of 175 L when filled with hydrogen at a pressure of 1 bar. Calculate the volume of the balloon when it rises to a height of 2000 m, where the atmospheric pressure is 0.80 bar. Assume that the temperature is constant.

3. A sample of gas at 20°C occupies a volume of 2 L at a pressure of 0.867×10^5 Pa. Calculate its volume at 100 kPa atmospheric pressure.

4. At a constant temperature, a gas occupies a volume of 200 mL at a pressure of 0.720 bar. It is subjected to an external pressure of 0.900 bar. What is the resulting volume of the gas ? ***N.C.E.R.T.***

5. A bulb of unknown volume V contains a gas at 1 atm pressure. This bulb was connected to another evacuated bulb of volume 0.5 L through a stop cock. When the stop cock was opened, the pressure at each bulb becomes 7.58×10^4 Pa mm while the temperature remained constant. Calculate V in litres.

6. A given mass of a gas occupies 4.5 dm^3 at 1.2 bar pressure. Calculate the change in volume of the gas at the same temperature if pressure of the gas is changed to 1.8 bar.

Answers to Practice Problems

1. 4.93 atm **2.** 218.75 L
3. 1.734 L **4.** 160 mL
5. 1.48 L **6.** 1.5 dm^3

Hints & Solutions on page 58

2. Charles' Law (Volume Temperature Relationship)

In 1787, a French scientist, Jacques Charles studied the effect of temperature on the volume of gases at constant pressure. The studies were extended by Gay Lussac in 1802. The following generalization about the relationship between volume and temperature of a gas was observed which is known as **Charles' law.** It states that,

at constant pressure, the volume of a given mass of a gas increases or decreases by 1/273 of its volume at 0°C for each one degree rise or fall in temperature.

Let V_0 be the volume of a given mass of a gas at 0°C and V_t is its volume at any temperature t°C, then the volume, V_t may be written in terms of Charles' law (*at constant pressure*) as :

For 1 degree rise in temperature, volume increases

$$= V_0 \times \frac{1}{273}$$

For t degree rise in temperature, volume increases

$$= V_0 \times \frac{1}{273} \times t$$

$\therefore$ Volume at t°C, V_t = Initial volume + Increase in volume

$$= V_0 + \frac{V_0 \times t}{273}$$

or $$V_t = V_0\left[1 + \frac{t}{273}\right]$$

Absolute or Kelvin scale of temperature. When a graph is plotted at constant pressure between volume (along y-axis) and temperature (along x-axis), a straight line is obtained. This is shown in Fig. 13. When the line is extrapolated to the lower temperature (shown by dotted line it touches the horizontal axis (temperature axis), which represents zero volume. The temperature at which volume becomes zero has been found to be –273°C (or exactly – 273.15°C). Charles knew that zero and negative values of volumes are not possible physically. Therefore, he proposed that –273°C is the lowest possible temperature. It may be noted that this value, –273°C does not depend upon the nature of gas or the pressure at which the experiment is performed. This can also be obtained from the above relation, as :

At t = –273°C; Volume $V = V_0\left[1 - \frac{273}{273}\right] = 0$

Thus, –273°C is the lowest possible temperature because below this temperature, the volume will become negative. This is meaningless. **This lowest temperature** is called **absolute zero temperature.** A British scientist, Lord Kelvin suggested a new scale of temperature based on this choice of temperature known as **absolute scale of temperature.** It is popularly known as the **Kelvin temperature scale.**

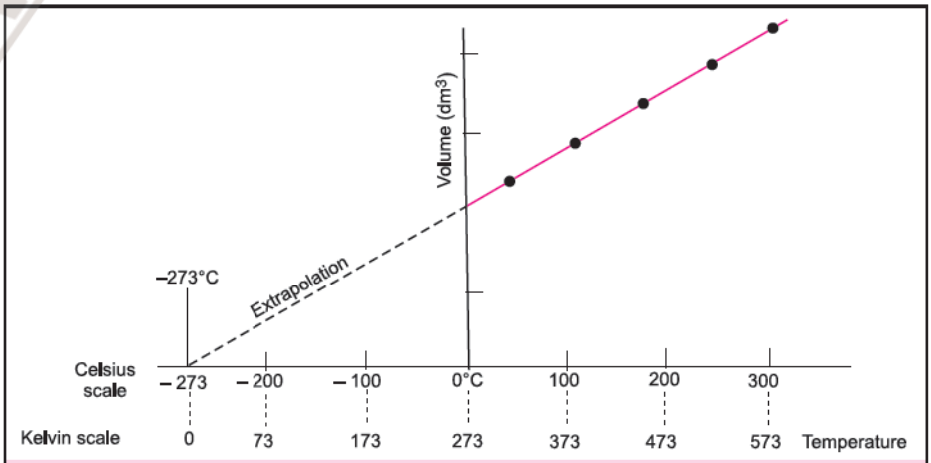

Fig. 13. A plot of volume versus temperature at constant pressure. The precise value of –273°C is – 273.15°C.

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Kelvin scale of temperature is also called **thermodynamic scale of temperature** and is used in all scientific measurements.

More careful experiments have shown that the absolute zero of temperature is –273.15°C. However, for most of the purposes, the approximate value of –273°C is used.

Temperatures on Kelvin scale are indicated simply by writing the letter K.

By convention, the degree sign (°) is not used while expressing the temperatures on the Kelvin scale.

Thus,

$$-273.15°C = 0\ K$$

or $$0°C = 273.15\ K$$

$$0°C = 273\ K\ (\text{For simplicity})$$

Similarly, $$1°C = (273 + 1)\ K = 274\ K$$

$$100°C = (273 + 100)\ K = 373\ K$$

In general, $$\boxed{t°C = (273 + t)\ K}$$

where t is the temperature on Celsius scale and T is the temperature on the Kelvin scale. Thus, temperature on Kelvin scale can be obtained by adding 273.15 (or approximately 273) to the temperature on Celsius scale. That is,

Kelvin temperature = Centigrade temperature + 273

$$T\,(K) = t\,(°C) + 273$$

As discussed above, gases occupy zero volume at 0K. However, no such phenomenon has ever been observed because all gases change to liquids or solids before this temperature is reached.

Alternative form of Charles' law. The absolute temperature scale has helped to simplify the relationship between temperature and gaseous volume. According to Charles' law given earlier, the volume of a given mass of a gas at temperature t°C is related to its volume at 0°C (*i.e.*, V_0) as

$$V_t = V_0\left(1 + \frac{t}{273}\right)$$

$$= V_0\left(\frac{273 + t}{273}\right)$$

But $273 + t = T(K)$ and $273 = T_0$ (say) which corresponds to 0°C on absolute temperature scale.

$$\therefore \quad V_t = \frac{V_0 T}{T_0}$$

or $$\frac{V_t}{V_0} = \frac{T}{T_0}$$

or $$\frac{V_t}{T} = \frac{V_0}{T_0}$$

Thus, $$\frac{V}{T} = \text{constant} = k_2$$

where k_2 is a constant which depends upon the pressure and the mass of the gas. It also depends upon the units of volume.

The above relation may be written as :

$$V = k_2 T$$

or $$V \propto T$$

Thus, **Charles' law** may also be stated as

pressure remaining constant the volume of a fixed mass of a gas is directly proportional to the absolute temperature.

Thus, if V_1 is the volume of a certain mass of a gas at temperature T_1 and V_2 is the volume of the same mass of the same gas at temperature T_2 at constant pressure, then according to Charles' law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}\ (\text{mass and pressure constant})$$

Experimental verification of the law

The validity of Charles' law can be experimentally demonstrated by determining volumes of a given mass of a gas at different temperatures keeping the pressure constant. Table 2 gives the volumes and temperatures for a certain gas at a constant pressure.

Table 2. Volume-temperature data for a given mass of a gas at a constant pressure.

Temperature (T) (K)	Volume (V) (*ml*)	(V/T) (*ml*/K)
273	800	2.93
293	858	2.93
323	946	2.93
333	982	2.95
353	1034	2.93
373	1096	2.91

It is clear from the table that value of V/T remains practically constant and this demonstrates the validity of the Charles' law.

Graphical representation of the law

This law can be illustrated by volume-temperature graph. At constant pressure, when a graph is plotted between volume V (along y-axis) and temperature (in Celsius) (along x-axis) straight lines are observed. On extending these lines to zero volume, each line intercepts the temperature axis at –273.15°C. Slopes of lines obtained at different pressures are different (Fig. 14) but at zero volume, all lines meet at the temperature axis at –273.15°C.

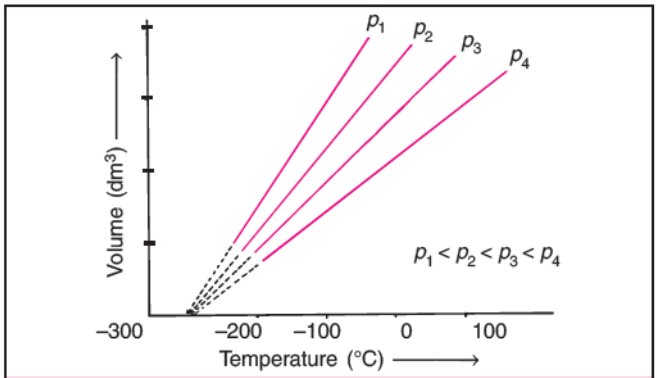

Fig. 14. Volume vs temperature (°C) graphs illustrating Charles' law.

However, when the graph is plotted as volume vs temperature, (temperature in Kelvin scale), a straight line is also obtained passing through the origin as shown in Fig. 15.

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The curves showing the volume temperature behaviour plotted at different fixed pressures are called **isobars.**

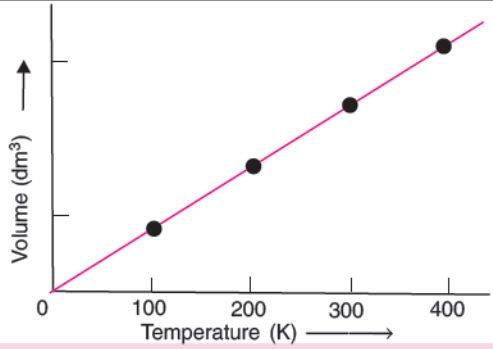

Fig. 15. Plot of volume versus temperature (K) to demonstrate Charles' law.

Practical significance of Charles' law

One of the interesting applications of Charles' law is the use of hot air balloons in sports and for meteorological observations. According to Charles' law, gases expand on heating. Since the mass of the gas sample is constant, the larger volume at higher temperature will have lower mass per unit volume and, therefore, lower density. Thus, hot air is less dense than cool air. This causes a hot air balloon to rise by displacing cool air (more dense) of the atmosphere. On this principle, *hydrogen balloons (which rise higher because of lower density of hydrogen) were developed as a means of transportation across the Atlantic.* However, *such airships are not being used because hydrogen is inflammable and the transportation will be risky.* But hydrogen balloons and hot air balloons are still being used for weather observations.

SOLVED EXAMPLES

❑ Example 5.

A sample of gas occupies 1.50 L at 25°C. If the temperature is raised to 60°C, what is the new volume of the gas if pressure remains constant?

Solution: $V_1 = 1.50$ L $\quad V_2 = ?$

$T_1 = 273 + 25 = 298$ K

$T_2 = 60 + 273 = 333$ K

Since pressure remains constant, therefore, by applying Charles' law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

or $$V_2 = \frac{V_1 T_2}{T_1} = \frac{(1.50\text{ L}) \times (333\text{ K})}{(298\text{ K})} = \mathbf{1.68\ L}$$

❑ Example 6.

A sample of helium has volume of 520 mL at 100°C. Calculate the temperature at which the volume will become 260 mL. Assume that pressure is constant.

Solution: $V_1 = 520$ mL $\quad V_2 = 260$ mL

$T_1 = 100 + 273 = 373$ K $\quad T_2 = ?$

Since pressure remains constant, therefore, by applying Charles' law :

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

or $$T_2 = \frac{V_2 \times T_1}{V_1}$$

$$\therefore \quad T_2 = \frac{(260\text{ mL}) \times (373\text{K})}{(520\text{ mL})}$$

$T_2 = 186.5$ K

or $t = 186.5 - 273 = \mathbf{-86.5°C}$

❑ Example 7.

At what centigrade temperature will a given volume of a gas at 0°C become double its volume, pressure remaining constant ?

Solution: Let the volume of the gas at 0°C be V.

$V_1 = V$

$T_1 = 273 + 0 = 273$ K

$V_2 = 2V$

$T_2 = ?$

Since pressure remains constant, therefore, by applying Charles' law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{V}{273} = \frac{2V}{T_2}$$

$$T_2 = \frac{2V \times 273}{V} = 546\text{ K}$$

Changing the temperature to centigrade scale,

Temperature = 546 – 273 = **273°C.**

❑ Example 8.

On a ship sailing in a pacific ocean where temperature is 23.4°C, a balloon is filled with 2L air. What will be the volume of the balloon when the ship reaches Indian ocean, where temperature is 26.1°C ? ***N.C.E.R.T.***

Solution: According to Charles' law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$V_1 = 2$L $\quad V_2 = ?$

$T_1 = 273 + 23.4 = 296.4$ K $\quad T_2 = 273 + 26.1 = 299.1$

$$\therefore \quad V_2 = \frac{V_1 T_2}{T_1}$$

$$= \frac{2\text{L} \times 299.1\text{K}}{296.4\text{K}} = \mathbf{2.018\ L}$$

❑ Example 9.

What is the increase in volume when the temperature of 800 mL of air increases from 27°C to 47°C under constant pressure of 1 bar ? ***N.C.E.R.T.***

Solution: Since the amount of gas and the pressure remains constant, Charles' law is applicable. *i.e.*

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$V_1 = 800$ mL $\quad V_2 = ?$

$T_1 = 273 + 27 = 300$ K $\quad T_2 = 273 + 47 = 320$ K

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$$\frac{800\ mL}{300\ K} = \frac{V_2}{320\ K}$$

or $$V_2 = \frac{(800\ mL)}{(300\ K)} \times (320\ K)$$

$$= 853.3\ mL$$

∴ Increase in volume of air = 853.3 – 800 = **53.3 mL**

❑ **Example 10.**

A cylinder containing cooking gas can withstand a pressure of 14.9 atmospheres. The pressure gauge of the cylinder indicates 12 atmosphere at 27°C. Due to sudden fire in the building, temperature starts rising. At what temperature will the cylinder explode ?

Solution: Since gas is confined in a cylinder, its volume will remain constant

Initial conditions	*Final conditions*
$p_1 = 12$ atm	$p_2 = 14.9$ atm
$T_1 = 273 + 27 = 300$ K	$T_2 = ?$

At constant volume

$$\frac{p_1}{T_1} = \frac{p_2}{T_2} \quad \text{or} \quad T_2 = \frac{p_2 T_1}{p_1}$$

$$= \frac{14.9 \times 300}{12.0} = 372.5\ K$$

or Temperature at which cylinder explodes

= 372.5 – 273 = **99.5°C.**

Practice Problems

7. 325 mg of a gas has a volume of 0.5 dm^3 at –10°C and 1 bar pressure. What will be the volume of the gas at 10°C at the same pressure?

8. It is desired to increase the volume of 800 ml of a gas by 20% keeping the pressure constant. To what temperature the gas be heated, if the initial temperature is 22°C?

9. At what temperature on Celsius scale will the volume of a given mass of a gas at 0°C become half of its volume at constant pressure?

10. A sample of air occupies 10 L at 127°C and 1 atm pressure. What volume of air will be expelled when it is cooled to –23°C at the same pressure ?

Answers to Practice Problems

7. 0.538 dm^3

8. 354 K

9. 136.5 K

10. 3.75 L

Hints & Solutions on page 58

3. Gay Lussac's Law (Pressure – Temperature Relationship)

The relationship between pressure and temperature was given by Joseph Gay Lussac and is known as **Gay Lussac's law.** It states that

at constant volume, pressure of a fixed amount of gas varies directly with temperature.

Mathematically, it may be expressed as

$$p \propto T$$

or $$\frac{p}{T} = \text{constant} = k_3$$

or $$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

This relationship can be derived from Boyle's law and Charles' law.

Graphical representation of the law. This law can be illustrated by pressure-temperature graph. At constant molar volume, when a graph is plotted between pressure and absolute temperature, straight lines are obtained as shown in Fig. 16

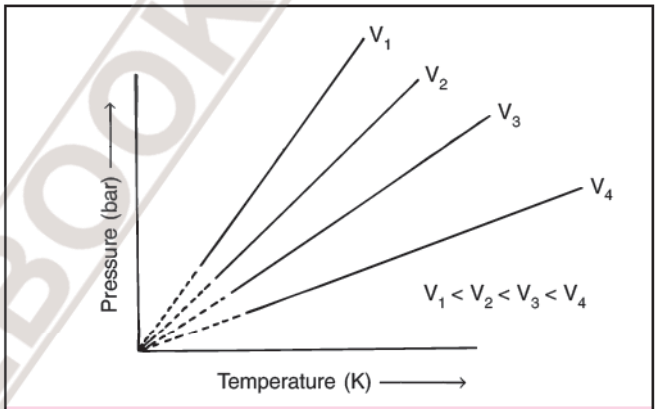

Fig. 16. Pressure versus temperature (K) graphs at different volumes (isochores) of a gas.

The curves showing the pressure temperature behaviour plotted at fixed volumes are called **isochores.**

Physical significance of Gay Lussac's law

Pressure in a well inflated tyres of automobiles is almost constant. But on hot summer day this increases considerably and tyre may burst, if pressure is not adjusted properly. Similarly, during winters, on a cold morning we find the pressure in the tyres of a vehicle decreased considerably.

SOLVED EXAMPLES

❑ **Example 11.**

A chamber of constant volume contains hydrogen gas. When the chamber is immersed in a bath of melting ice (0°C), the pressure of the gas is 1.07 × 10^2 kPa. What pressure will be indicated when the chamber is brought to 100°C ? ***N.C.E.R.T.***

Solution: $T_1 = 273 + 0 = 273$ K,

$p_1 = 1.07 \times 10^2$ kPa

$= 107$ kPa

$T_2 = 273 + 100 = 373$ K, $p_2 = ?$

Since volume remains constant, therefore, according to Gay Lussac's law:

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$$\frac{p_1}{T_1} = \frac{p_2}{T_2} \quad \text{or} \quad p_2 = \frac{p_1 T_2}{T_1}$$

$$= \frac{(107\ \text{kPa}) \times (373\ \text{K})}{(273\ \text{K})}$$

$$= \mathbf{1.462 \times 10^2\ kPa.}$$

4. Avogadro's Law (Volume–Amount Relationship)

Amadeo Avogadro in 1811, put forward a relationship between volume of a gas to the number of molecules at constant temperature and pressure. This has now been accepted as a law and is known as **Avogadro law.** The law states that,

equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.

This means that as long as the temperature and pressure remain constant, the volume of the gas depends upon the number of molecules of the gas or amount of the gas.

Mathematically, Avogadro's law may be expressed as :

$$V \propto n \ (p \text{ and } T \text{ constant})$$

or $$V = k_4 n$$

where 'n' is the amount of substance (moles).

The number of molecules in one mole of a gas has been determined to be 6.022×10^{23} and is known as **Avogadro constant.**

This means that one mole of each gas at standard temperature and pressure will have the same volume. This is known as molar volume, V_m.

Molar volume of the gas under different conditions

(*i*) **Standard conditions of temperature and pressure (STP) :** Under standard conditions of temperature 0°C (273.15 K) and one atmospheric pressure, molar volume, i.e. volume occupied by 1 mol of a gas is **22.4 L mol^{-1}**.

However, if the standard conditions used are 0°C (273.15 K) temperature and 1 bar pressure (10^5 Pa), molar volume i.e. volume of gas occupied by 1 mol of a gas is **22.71 L mol^{-1}**.

(*ii*) **Standard ambient temperature and pressure (SATP) conditions:** The standard ambient conditions are also used in some scientific work. These are 298.15 K temperature and 1 bar (10^5 Pa) pressure. At SATP conditions, molar volume i.e. volume occupied by 1 mol of a gas is **24.789 L mol^{-1}**.

Molar volumes of some gases are given in Table 3.

Table 3. Molar volume in litres per mole of some gases at 273.15 K and 1 atm pressure (STP).

Gas	Molar volume
Argon	22.37
Carbon dioxide	22.54
Dinitrogen	22.69
Dioxygen	22.69
Dihydrogen	22.72
Ideal gas	22.71

REMEMBER

It may be noted that

- when STP conditions taken are 0°C and 1 atm pressure,

molar volume of the gas = 22.4 L mol^{-1}

- when STP conditions taken are 0°C (273.15K) and 1 bar pressure,

molar volume of the gas = 22.71 L mol^{-1}

- when SATP conditions taken are 25°C (298.15K) and 1 bar pressure,

molar volume of the gas = 24.789 L mol^{-1}

Now, number of moles of a gas can be calculated as :

$$n = \frac{\text{Mass of gas}}{\text{Molar mass}} = \frac{m}{M}$$

Thus, $$V = k_4 \frac{m}{M}$$

This can be rearranged as :

$$M = k_4 \frac{m}{V} = k_4 d$$

where 'd' is density of the gas. Thus, we can say that *the density of a gas is directly proportional to its molar mass.*

A gas which obeys Boyle's law, Charles' law and Avogadro law strictly is called **ideal gas.** Such a gas is hypothetical. It is based on the assumption that intermolecular forces are not present between the molecules of an ideal gas. However, real gases do not obey these laws at all conditions. This will be learnt later.

5. The Combined Gas Law or Ideal Gas Equation

Boyle's and Charles' laws give separately variation of the volume of a gas with pressure and temperature respectively. By combining these two laws, we get an equation which gives the simultaneous effect of the changes of pressure and temperature on the volume of the gas. This is known as **combined gas law** or **gas equation.**

Consider a known quantity of a gas at pressure p_1, temperature T_1 and having a volume V_1. Suppose that it is to be converted to another state having pressure p_2, volume V_2 and temperature T_2. The gas equation can be derived as follows :

Step I. Let us change the pressure of the gas from p_1 to p_2 at a constant temperature T_1 the volume will change from V_1 to new volume say V_x (Fig. 17). Since temperature remains constant, therefore, by applying Boyle's law,

$$p_1 V_1 = p_2 V_x \qquad \ldots(i)$$

or $$V_x = \frac{p_1 V_1}{p_2}$$

Step II. Let the temperature of the gas be now changed to T_2 at constant pressure p_2 so that volume may change from V_x to V_2. Thus, according to Charles' law,

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$$\frac{V_x}{T_1} = \frac{V_2}{T_2} \quad \text{or} \quad V_2 = \frac{V_x T_2}{T_1} \qquad ...(ii)$$

Substituting the value of V_x from Eq. (*i*), we get

$$V_2 = \frac{p_1 V_1}{p_2} \times \frac{T_2}{T_1}$$

Rearranging, we get

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

Thus, $$\frac{pV}{T} = \text{Constant (K)}$$

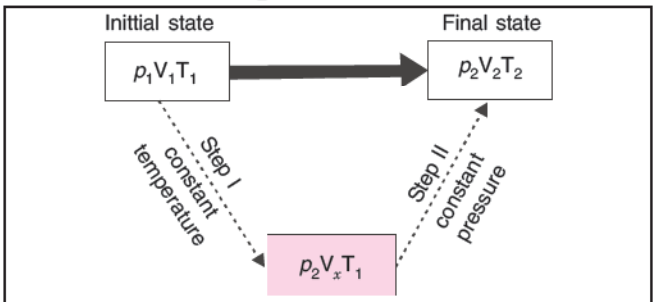

Fig. 17. Steps involved in change of one state to another.

This is known as *combined gas law*. This can be used to calculate unknown variable. Knowing any five variables, the sixth can be calculated.

Alternative Derivation for the Gas Equation

Gas equation can also be derived by combining Boyle's and Charles' laws as given below :

According to Boyle's law, for a fixed mass of a gas at constant temperature

$$V \propto \frac{1}{p} \quad \text{(Constant T and } n\text{)} \qquad ...(i)$$

According to Charles' law,

$$V \propto T \quad \text{(Constant } p \text{ and } n\text{)} \qquad ...(ii)$$

According to Avogadro's law

$$V \propto n \quad \text{(Constant } p \text{ and T)} \qquad ...(iii)$$

Combining equations (*i*), (*ii*) and (*iii*), the combined gas law can be written as :

$$V \propto \frac{nT}{p}$$

or $$pV \propto nT \text{ or } pV = nRT$$

where R is a constant of proportionality and is known as **molar gas constant.** The value of R is same for all gases. Therefore, it is also called **universal gas constant.** However, the numerical value of R varies with the units in which pressure and volume are expressed.

For one mole of gas ($n = 1$)

$$\boldsymbol{pV = RT}$$

The above equation is known as **ideal gas equation.** The word *ideal* is used because there is no actual gas which completely obeys this equation. However, the real gases behave ideally at high temperatures and low pressures. Since the ideal gas equation expresses the quantitative relationship between the four variables that describe the state of a gas, it is also known as **equation of state** for gases.

Nature of Universal Gas Constant 'R'

In order to understand the significance of R, let us examine the nature of quantities in the ideal gas equation :

$$pV = nRT$$

$$R = \frac{pV}{nT}$$

i.e. $$R = \frac{\text{Pressure} \times \text{Volume}}{\text{Moles} \times \text{Temperature}}$$

Since, pressure is force per unit area.

$$\therefore \quad R = \frac{\frac{\text{Force}}{\text{Area}} \times \text{Volume}}{\text{Moles} \times \text{Temperature}}$$

Since area = $(\text{length})^2$ and volume = $(\text{length})^3$, so that

$$R = \frac{\frac{\text{Force}}{(\text{Length})^2} \times (\text{Length})^3}{\text{Moles} \times \text{Temperature}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Moles} \times \text{Temperature}}$$

But Force × Length = Work

$$\therefore \quad R = \frac{\text{Work}}{\text{Moles} \times \text{Temperature}}$$

Thus, **R represents work done per degree per mol or energy per degree per mole.**

Since work can be expressed in different systems of units, R will have different values in different systems.

Numerical values of R. The numerical value of R depends upon the units in which pressure and volume are expressed.

(i) When pressure is expressed in atmosphere and volume in litres, the value of R comes out to be in *litre-atmosphere per degree per mole.*

From the general gas equation,

$$R = \frac{P \times V}{n \times T}$$

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We know that 1 mole of any gas at S.T.P. (1 atm pressure and 273 K) occupies a volume of 22.4 L.

Substituting these values,

$$R = \frac{(1\text{ atm}) \times (22.4\text{ L})}{(1\text{ mole}) \times (273\text{ K})}$$

$$= \mathbf{0.0821\ L\ atm\ K^{-1}\ mol^{-1}}$$

(ii) When pressure is expressed in atmosphere and volume in millilitres (ml).

We know that one mole of a gas at S.T.P. (1 atm pressure and 273 K) occupies a volume of 22,400 *ml*. Then

$$R = \frac{(1\text{ atm}) \times (22400\text{ mL})}{(1\text{ mole}) \times (273\text{ K})}$$

$$= \mathbf{82.1\ atm\ mL\ K^{-1}\ mol^{-1}}$$

(iii) When pressure is expressed as Pa and volume in m^3, then R is expressed as Joule per degree per mol.

We know that 1 mole of a gas at STP (1 bar pressure and 273.15 K) occupies 22.7×10^{-3} m^3. Then

$$R = \frac{(10^5\text{Pa}) \times (22.7 \times 10^{-3}\ \text{m}^3)}{(1\text{ mol}) \times (273.15\text{ K})}$$

$$= \frac{10^5\text{ Nm}^{-2} \times 22.7 \times 10^{-3}\ \text{m}^3}{1\text{ mol} \times 273.15\text{ K}}$$

$$= 8.314\text{ Nm mol}^{-1}\text{ K}^{-1}$$

$$= \mathbf{8.314\ J\ mol^{-1}\ K^{-1}}\ (\because \text{Nm} = \text{J})$$

(iv) When pressure is expressed in bar and volume in dm^3, then R is expressed as bar dm^3 mol^{-1} K^{-1}.

We know that 1 mol of a gas at STP (1 bar pressure and 273.15 K) occupies 22.7 dm^3. Then

$$R = \frac{(1\text{ bar}) \times (22.7\text{ dm}^3)}{(1\text{ mol}) \times (273.15\text{ K})}$$

$$= \mathbf{0.0831\ bar\ dm^3\ mol^{-1}\ K^{-1}}$$

The different values of R in terms of different units of pressure and volume are given in Table 4.

Table 4. Value of universal gas constant R in different units.

Units required V	p	R value
L	atm	0.0821 L atm K^{-1} mol^{-1}
mL	atm	82.1 mL atm K^{-1} mol^{-1}
L	bar	0.08314 L bar K^{-1} mol^{-1}
dm^3	bar	0.08314 dm^3 bar K^{-1} mol^{-1}
m^3	Pa*	8.314 Pa m^3 K^{-1} mol^{-1}
		or 8.314 Nm K^{-1} mol^{-1}
	or Nm^{-2}	or 8.314 J K^{-1} mol^{-1}

*Pa = Nm^{-2} and Pa m^3 = 1 J = 1 kg m^2 s^{-2}

It may be noted that although R may be expressed in different units, but for pressure-volume calculations, R must be taken in the same units as those used for pressure and volume.

SOLVED EXAMPLES

Example 12.

A sample of nitrogen occupies a volume of 1.0 L at a pressure of 0.5 bar at 40°C. Calculate the pressure if the gas is compressed to 0.225 mL at –6°C.

Solution: $p_1 = 0.5$ bar $\quad p_2 = ?$

$V_1 = 1.0$ L $\quad V_2 = 0.225$ mL $= 0.225 \times 10^{-3}$ L

$T_1 = 273 + 40 = 313$ K

$T_2 = 273 - 6 = 267$ K

According to gas equation,

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

$$p_2 = \frac{p_1V_1T_2}{V_2T_1}$$

$$= \frac{0.5\text{ bar} \times 1.0\text{ L} \times 267\text{ K}}{0.225 \times 10^{-3}\text{ L} \times 313\text{ K}} = \mathbf{1895.6\ bar.}$$

Example 13.

At 25°C and 760 mm of Hg pressure, a gas occupies 600 mL volume. What will be its pressure at a height where temperature is 10°C and volume of the gas is 640 mL. ***N.C.E.R.T.***

Solution: $p_1 = 760$ mm Hg $\quad p_2 = ?$

$V_1 = 600$ mL $\quad V_2 = 640$ mL

$T_1 = 273 + 25 = 298$ K $\quad T_2 = 273 + 10 = 283$ K

According to combined gas law equation,

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

or $$p_2 = \frac{p_1V_1T_2}{V_2T_1}$$

$$= \frac{(760\text{ mm Hg}) \times (600\text{ mL}) \times (283\text{ K})}{(640\text{ mL})\ (298\text{K})}$$

$$= \mathbf{676.6\ mm\ Hg}$$

Example 14.

Calculate the moles of hydrogen (H_2) present in a 500 mL sample of hydrogen gas at a pressure of 1 bar and 27°C.

Solution: According to ideal gas equation,

$pV = nRT$

$p = 1$ bar, $V = 500$ mL $= 500 \times 10^{-3}$ dm^3

$T = 27 + 273 = 300$ K, $R = 0.083$ bar dm^3 K^{-1} mol^{-1}

Now, $$n = \frac{pV}{RT}$$

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$$n = \frac{1\text{ bar} \times 500 \times 10^{-3}\text{ dm}^3}{0.083\text{ bar dm}^3\text{ mol}^{-1}\text{ K}^{-1} \times 300\text{ K}}$$

$$= 0.0201\text{ mol} = \mathbf{2.01 \times 10^{-2}\ mol}$$

Example 15.

Calculate the volume occupied by 4.045×10^{23} molecules of oxygen at 27°C and having a pressure of 0.935 bar.

Solution: Here, number of molecules = 4.045×10^{23}

$p = 0.933$ bar

T = 27 + 273 = 300 K

R = 0.083 bar dm^3 mol^{-1} K^{-1}

Let us first calculate the number of moles, n. We know that number of moles,

$$n = \frac{\text{No. of molecules}}{6.022 \times 10^{23}} = \frac{4.045 \times 10^{23}}{6.022 \times 10^{23}} = 0.672\text{ mol}$$

Now, according to general gas equation,

$$pV = nRT \quad \text{or} \quad V = \frac{nRT}{p}$$

$$\therefore\ V = \frac{0.672\text{ mol} \times 0.083\text{ bar dm}^3\text{ K}^{-1}\text{ mol}^{-1} \times 300\text{ K}}{0.993\text{ bar}}$$

$$= \mathbf{17.93\ dm^3\ (or\ L)}$$

Example 16.

A discharge tube of 2 L capacity containing hydrogen gas was evacuated till the pressure inside is 1×10^{-5} atm. If the tube is maintained at a temperature of 27°C, calculate the number of hydrogen molecules still present in the tube.

Solution:

Step I. *To calculate the number of moles of hydrogen.*

Here $p = 1 \times 10^{-5}$ atm, V = 2 litres

R = 0.082 litre atm K^{-1} mol^{-1}

T = 27 + 273 = 300 K

n = ?

According to the gas equation,

$$pV = nRT \quad \text{or} \quad n = \frac{pV}{RT}$$

Substituting the values

$$\therefore\quad n = \frac{1 \times 10^{-5}\text{ atm} \times 2\text{ litres}}{0.082\text{ litre atm K}^{-1}\text{ mol}^{-1} \times 300\text{ K}}$$

$$= 8.1 \times 10^{-7}\text{ mol.}$$

Step II. *To calculate the number of hydrogen molecules.*

We know that

1 mol of hydrogen = 6.022×10^{23} molecules

8.1×10^{-7} mol of hydrogen $= 6.022 \times 10^{23} \times 8.1 \times 10^{-7}$

$$= \mathbf{4.879 \times 10^{17}\ molecules.}$$

Example 17.

Calculate the mass of 120 mL of N_2 at 150°C and 1×10^5 Pa pressure.

Solution: According to ideal gas equation,

$$pV = nRT = \frac{m}{M}RT$$

$$\left[\text{moles } (n) = \frac{\text{mass } (m)}{\text{molecular mass (M)}}\right]$$

or $$m = \frac{pVM}{RT}$$

$p = 10^5$ Pa = 10^5 Nm^{-2}, V = 120 $\times 10^{-6}$ m^3

M = 28, T = 273 + 150 = 423 K,

R = 8.314 Nm K^{-1} mol^{-1}

$$\text{Mass of gas, } m = \frac{10^5\text{ Nm}^{-2} \times 120 \times 10^{-6}\text{ m}^3}{8.314\text{ Nm mol}^{-1}\text{ K}^{-1} \times 423\text{ K}}$$

$$= \mathbf{0.0955\ g}$$

Example 18.

Calculate the volume occupied by 8.8 g of CO_2 at 31.1 °C and 1 bar pressure.
($R = 0.083$ bar dm^3 K^{-1} mol^{-1}.)

Solution: According to ideal gas equation,

$pV = nRT$

$$n = \frac{8.8}{44}\text{ mol}, \quad P = 1\text{ bar},$$

T = 273 + 31.1 = 304.1 K

V = ? R = 0.083 bar dm^3 K^{-1} mol^{-1}

$$\text{Now } V = \frac{nRT}{p}$$

$$= \frac{\left(\frac{8.8}{44}\text{ mol}\right) \times (0.083\text{ bar dm}^3\text{ K}^{-1}\text{ mol}^{-1}) \times (304.1\text{ K})}{1\text{ bar}}$$

$$= \mathbf{5.05\ dm^3}\text{ or }\mathbf{5.05\ L}$$

Example 19.

Calculate the volume occupied by 2 moles of an ideal gas at 2.5×10^5 Nm^{-2} pressure and 300 K temperature.

Solution: According to ideal gas equation,

$$pV = nRT \quad \text{or} \quad V = \frac{nRT}{p}$$

$n = 2$ mol, T = 300 K, $p = 2.50 \times 10^5$ Nm^{-2}

R = 8.314 Nm K^{-1} mol^{-1}

$$\therefore\quad V = \frac{2\text{ mol} \times 8.314\text{ Nm K}^{-1}\text{ mol}^{-1} \times 300\text{ K}}{2.5 \times 10^5\text{ Nm}^{-2}}$$

$$= 19.95 \times 10^{-3}\text{ m}^3 = \mathbf{19.95\ dm^3}$$

Example 20.

Calculate the temperature of 4.0 moles of a gas occupying 5 dm^3 at 3.32 bar ($R = 0.083$ bar dm^3 K^{-1} mol^{-1}). **N.C.E.R.T.**

Solution: According to ideal gas equation :

$$pV = nRT$$

$p = 3.32$ bar, V = 5 dm^3, $n = 4.0$ mol,

R = 0.083 bar dm^3 K^{-1} mol^{-1}

$$T = \frac{pV}{nR}$$

$$= \frac{3.32\text{ bar} \times 5\text{ dm}^3}{4.0\text{ mol} \times 0.083\text{ bar dm}^3\text{ K}^{-1}\text{ mol}^{-1}}$$

$$= \mathbf{50\ K.}$$

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❑ **Example 21.**

Pay load is defined as the difference between the mass of displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10 m, mass 100 kg is filled with helium at 1.66 bar at 27°C. (Density of air = 1.2 kg m^{-3} and R = 0.083 bar dm^3 K^{-1} mol^{-1}). **N.C.E.R.T.**

Solution: Pay load is the difference between the mass of displaced air and the mass of the balloon.

$$\text{Volume of ballon} = \frac{4}{3}\pi r^3$$

$$\text{Radius of balloon, } r = 10\text{m}$$

$$V = \frac{4}{3} \times 3.14 \times (10)^3 = 4186.7 \text{ m}^3$$

$$\text{Mass of displaced air} = 4186.7 \text{ m}^3 \times 1.2 \text{ kg m}^{-3} = 5024.04 \text{ kg}$$

$$\text{Moles of gas present} = \frac{pV}{RT} = \frac{1.66 \times 4186.7 \times 10^3}{0.083 \times 300} = 279.11 \times 10^3 \text{ mol}$$

$$\text{Mass of helium present} = 279.11 \times 10^3 \times 4 = 1116.44 \times 10^3 \text{ g} = 116.4 \text{ kg}$$

$$\text{Mass of filled balloon} = 100 + 1116.4 = 1216.4 \text{ kg}$$

$$\text{Pay load} = \text{mass of displaced air} - \text{Mass of balloon} = 5024.04 - 1216.44 = \mathbf{3807.6 \text{ kg.}}$$

❑ **Example 22.**

2.9 g of a gas at 95°C occupied the same volume as 0.184 g of hydrogen at 17°C at the same pressure. What is the molar mass of the gas ?

Solution: Let molar mass of gas is M.

$$\text{Moles of gas} = \frac{2.9}{M}, \quad T = 273 + 95 = 368 \text{ K}$$

$$\text{Volume of gas, } V = \frac{nRT}{p} = \frac{2.9 \times R \times 368}{M \times p}$$

$$\text{Moles of dihydrogen} = \frac{0.184}{2} = 0.092, \quad T = 273 + 17 = 290 \text{ K}$$

$$\text{Volume of dihydrogen} = \frac{0.092 \times R \times 290}{p}$$

$$\text{Volume of gas} = \text{Volume of dihydrogen at same pressure, } p$$

$$\frac{2.9 \times R \times 368}{M} = 0.092 \times R \times 290$$

$$\therefore \quad M = \frac{2.9 \times 368}{0.092 \times 290} = \mathbf{40.}$$

Density and molar mass of a gaseous substance.

Molar mass of an ideal gas can be calculated from the ideal gas equation as :

$$pV = nRT \quad \text{or} \quad p = \frac{nRT}{V}$$

Now, number of moles (n)

$$= \frac{\text{Mass of substances } (m)}{\text{Molar mass (M)}}$$

$$\therefore \quad p = \frac{m\,RT}{MV}$$

But mass per unit volume is density, *i.e.*

$$\frac{m}{V} = d; \text{ where } d \text{ is the the density of gas.}$$

$$p = \frac{dRT}{M} \text{ or } M = \frac{dRT}{p}$$

This relation can be used to calculate molar mass of a gaseous substance.

❑ **Example 23.**

The drain cleaner contains small bits of aluminium which react with caustic soda to produce dihydrogen gas. What volume of dihydrogen at 20°C and one bar pressure will be released when 0.15 g of aluminium reacts ?

N.C.E.R.T.

Solution:

$$\underset{2 \times 27 = 54}{2Al} + 2\,NaOH + 2H_2O \longrightarrow 2\,NaAlO_2 + \underset{3 \times 22.4 \text{ L}}{3H_2}$$

It is known that 1 mol of any gas at 0°C and 1 bar pressure occupies 22.4 L

54 g of Al give $H_2 = 3 \times 22.4$ L

$$0.15 \text{ g of Al will give } H_2 = \frac{3 \times 22.4}{54} \times 0.15 = 0.189 \text{ L}$$

So, 0.189 L of H_2 will be released at 1 bar pressure and 273 K. To calculate volume of H_2 at 20°C and 1 bar pressure,

$p_1 = 1$ bar $\quad p_2 = 1$ bar

$V_1 = 0.189$ L $\quad V_2 = ?$

$T_1 = 273$ K $\quad T_2 = 273 + 20 = 293$ K

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \text{ or } V_2 = \frac{p_1V_1 \times T_2}{p_2 \times T_1}$$

$$\therefore \quad V_2 = \frac{1 \text{ bar} \times 0.189 \times 293 \text{ K}}{1 \text{ bar} \times 273 \text{ K}}$$

$$= 0.2028 \text{ L} = \mathbf{202.8 \text{ mL}}$$

❑ **Example 24.**

The density of a gas at 27°C and 1 bar pressure is 2.56 g L^{-1}. Calculate the molar mass.

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Solution: We are given
p = 1.0 bar, T = 27 + 273 = 300 K,
d = 2.56 g L^{-1} or 2.56 g dm^{-3}
We know that

$$M = \frac{dRT}{p}$$

Where R = 0.083 bar dm^3 mol^{-1} K^{-1}

$$M = \frac{2.56 \text{ g dm}^{-3} \times 0.083 \text{ bar dm}^3 \text{ mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{1 \text{ bar}}$$

$$= 63.74 \text{ g mol}^{-1}$$

Molar mass of gas = 63.74.

❑ Example 25.

The mass of 525 ml of a gaseous compound at 28°C and 0.970 bar pressure was found to be 0.900 g. Calculate the molar mass of the compound.

Solution: According to ideal gas equation,

$$pV = nRT \quad \text{or} \quad pV = \frac{m}{M}RT$$

where m = mass of gas, M = molar mass

$$\therefore \quad M = \frac{mRT}{pV}$$

p = 0.970 bar, V = 525 mL = 525 × 10^{-3} dm^3
T = 273 + 28 = 301 K
R = 0.083 bar dm^3 mol^{-1} K^{-1}
m = 0.900 g
Substituting the values,

$$M = \frac{0.900 \text{ g} \times 0.083 \text{ bar dm}^3 \text{ mol}^{-1} \text{ K}^{-1} \times 301 \text{ K}}{0.970 \text{ bar} \times 525 \times 10^{-3} \text{ dm}^3}$$

$$= 44.1 \text{ g mol}^{-1}$$

$\therefore$ **Molar mass = 44.1**

❑ Example 26.

Density of a gas is found to be 5.46 g dm^{-3} at 27°C and 2 bar pressure. What will be its density at STP ?

Solution: We know that

$$pV = nRT$$

or $$p = \frac{m}{V} \times \frac{RT}{M} = \frac{dRT}{M}$$

$$\therefore \quad d = \frac{pM}{RT}$$

or $$d \propto \frac{p}{T} \text{ (R and M constant for a given gas)}$$

or $$\frac{d_1}{d_2} = \frac{p_1}{p_2} \times \frac{T_2}{T_1}$$

or $$d_2 = \frac{d_1 \times p_2 \times T_1}{p_1 \times T_2},$$

d_1 = 5.46 g dm^{-3}, p_1 = 2 bar
T_1 = 273 + 27 = 300 K
d_2 = ? p_2 = 1 bar T_2 = 273 K

$$\therefore \quad d_2 = \frac{5.46 \text{ g dm}^{-3} \times 1 \text{ bar} \times 300 \text{ K}}{2 \text{ bar} \times 273 \text{ K}}$$

$$= \mathbf{3.0 \text{ g dm}^{-3}}$$

❑ Example 27.

At 273 K, the density of a gaseous oxide at 2 bar is same as that of nitrogen at 5 bar. Calculate the molecular mass of oxide. ***N.C.E.R.T.***

Solution: $d = \frac{pM}{RT}$

For nitrogen gas at 5 bar pressure and 273 K temperature

$$d(N_2) = \frac{5 \text{ bar} \times 28 \text{ g mol}^{-1}}{R \times 273 \text{ K}}$$

For gaseous oxide at 2 bar pressure and 273 K temperature

$$d(\text{oxide}) = \frac{2 \text{ bar} \times M \text{ g mol}^{-1}}{R \times 273 \text{ K}}$$

Now $d(N_2) = d(\text{oxide})$

$$\frac{5 \text{ bar} \times 28 \text{ g mol}^{-1}}{R \times 273 \text{ K}} = \frac{2 \text{ bar} \times M \text{ g mol}^{-1}}{R \times 273 \text{ K}}$$

$$\therefore \quad M = \frac{5 \times 28}{2} = \mathbf{70 \text{ g mol}^{-1}}$$

❑ Example 28.

Calculate the density of ammonia (NH_3) at 30°C and 5 bar pressure.

Solution: $pV = nRT$ or $p = \frac{m}{V} \times \frac{RT}{M} = \frac{dRT}{M}$

$$\therefore \quad d = \frac{pM}{RT}$$

P = 5 bar, T = 273 + 30 = 303 K, M = 17,
R = 0.083 bar dm^3 mol^{-1} K^{-1}.

$$\therefore \quad d = \frac{(5 \text{ bar}) \times (17 \text{ g mol}^{-1})}{(0.083 \text{ bar dm}^3 \text{ mol}^{-1} \text{ K}^{-1}) \times (303 \text{ K})}$$

$$= \mathbf{3.37 \text{ g dm}^{-3}}$$

Practice Problems

11. How much time would it take to distribute one Avogadro number of wheat grains if 10^{10} grains are distributed each second ? ***N.C.E.R.T.***

12. A sample of oxygen gas occupies 431 mL at standard temperature and pressure. Calculate the volume when the temperature is 35°C and pressure is 1.05 bar.

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13. Ten grams of oxygen are introduced into an evacuated vessel of 5 dm^3 capacity maintained at 26°C. Calculate the pressure (R = 0.083 bar dm^3 mol^{-1} K^{-1})

14. The density of liquid CO_2 at room temperature is 0.8 g cm^{-3}. How large a cartridge of liquid CO_2 must be provided to inflate a life jacket of 4 litres capacity at S.T.P.?

15. 150 mL of a gas at N.T.P. were taken to 20°C and 0.96 bar pressure. What is the change in volume of the gas ?

16. Calculate the number of molecules in a sample of an ideal gas whose volume is 0.45 L at 67°C and 0.76 bar pressure.

17. The density of phosphine gas is 1.27 g dm^{-3} at 50°C and 0.987 × 10^5 Pa. Calculate its molar mass.

18. The density of oxygen is 1.43 g dm^{-3} at STP. Determine its density at 17°C and 800 torr pressure.

19. 34.05 mL of phosphorus vapour weigh 0.0625 g at 546°C and 1.0 bar pressure. What is the molecular mass of phosphorus? How many atoms are there in one molecule of phosphorus ? ***N.C.E.R.T.***

20. A closed tank is first evacuated and then connected to a 50 L cylinder containing compressed nitrogen gas. The gas pressure in the cylinder originally at 20.5 bar falls to 11.2 bar after it is connected to the evacuated tank. Calculate the volume of the tank.

21. 18g mixture of helium and argon occupied 30L at 1 atm pressure and 27°C. Calculate the percentage of these gases in the mixture.

22. A student forgot to add the reaction mixture to the round bottomed flask at 27°C but put it on the flame. After a lapse of time, he realised his mistake and found the temperature of the flask was 477°C. What fraction of air would have been expelled out ?

N.C.E.R.T.

23. 2.9 g of a gas at 95°C occupies the same volume as 0.184 g of hydrogen at 17°C at the same pressure. Calculate the molar mass of the gas.

24. 3.7 g of a gas at 25°C occupied the same volume as 0.184 g of H_2 gas at 17°C and at the same pressure. What is the molar mass of gas ?

25. 20% N_2O_4 molecules are dissociated in a sample of gas at 27°C and 760 torr as :

$$N_2O_4 \rightleftharpoons 2NO_2$$

Calculate the density of the equilibrium mixture.

Answers to Practice Problems

11.	1.9096×10^6 years	**12.**	463.1 mL
13.	1.55 bar	**14.**	9.82 cm^3
15.	17.7 mL increase	**16.**	7.3×10^{21}
17.	35.01 g mol^{-1}	**18.**	1.417 g/L
19.	4	**20.**	41.5 L
21.	18.95, 81.05	**22.**	$\frac{3}{5}$
23.	40 g mol^{-1}	**24.**	41.3
25.	3.11 gL^{-1}		

Hints & Solutions on page 58

6. Dalton's Law of Partial Pressures

This law was formulated by John Dalton in 1801. It deals with the pressure exerted by a mixture of non-reacting gases enclosed in a vessel. **Dalton's law of partial pressures** states that

the total pressure exerted by a mixture of two or more non-reacting gases in a definite volume is equal to the sum of the individual pressures which each gas would exert if it occupies the same volume alone at a constant temperature.

For example, if p_1, p_2, p_3 ... are individual pressures of gases known as *partial pressures,* then the total pressure p_{total} of the mixture of gases at the same temperature is given by the following relation :

$$p_{total} = p_1 + p_2 + p_3 + ...$$

The partial pressure of each gas means the pressure which that gas would exert if present alone in the vessel at the same temperature as that of the mixture.

Illustration of the Dalton's law of partial pressures. To demonstrate the law, let us consider

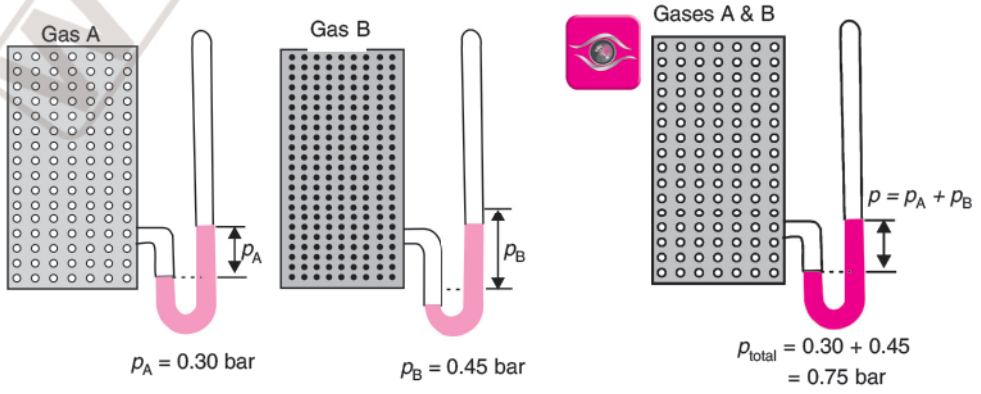

Fig. 18. Illustration of Dalton's law of partial pressures.

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three vessels each of 1 litre capacity. Let the first vessel contains a gas 'A' having a pressure 0.30 bar and the second contains a gas 'B' having a pressure 0.45 bar. Now, if we put both the gases A and B in the third vessel at the same temperature, the total pressure in the third vessel would be

$$p_{total} = p_A + p_B$$
$$= 0.30 \text{ bar} + 0.45 \text{ bar}$$
$$= 0.75 \text{ bar}$$

This is shown in Fig. 18.

Partial pressure in terms of mole fraction

Mole fraction is a method of expressing concentration of a component in a mixture. It is defined as *the moles of a substance in a mixture as a fraction of total moles of all substances.* If n_1 moles of any substance is present in n moles of the mixture, then mole fraction x_1 of the substance,

$$x_1 = \frac{n_1}{n}$$

For example, for a mixture of two substances A and B having moles n_A and n_B respectively, then their mole fractions are :

$$x_A = \frac{n_A}{n_A + n_B} \quad \text{or} \quad x_B = \frac{n_B}{n_A + n_B}$$

Suppose at temperature T, three gases enclosed in the volume V exert partial pressure p_1, p_2 and p_3 respectively. Then

$$p_1 = \frac{n_1 RT}{V}$$

$$p_2 = \frac{n_2 RT}{V}$$

$$p_3 = \frac{n_3 RT}{V}$$

Where n_1, n_2 and n_3 are the number of moles of these gases. Thus,

$$p_{total} = p_1 + p_2 + p_3$$
$$= n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + n_3 \frac{RT}{V}$$
$$= (n_1 + n_2 + n_3) \frac{RT}{V}$$

On dividing p_1 by p_{total}, we get

$$\frac{p_1}{p_{total}} = \left(\frac{n_1}{n_1 + n_2 + n_3}\right) \frac{RT}{V} \times \frac{V}{RT}$$

But $\frac{n_1}{n_1 + n_2 + n_3} = \frac{n_1}{n} = x_1$

$(\because n_1 + n_2 + n_3 = \text{total number of moles} = n)$

where x_1, is the mole fraction of first gas. Thus,

$$\frac{p_1}{p_{total}} = x_1 \text{ or } p_1 = x_1 \, p_{total}$$

Similarly for other two gases,

$$p_2 = x_2 \, p_{total} \text{ and } p_3 = x_3 \, p_{total}$$

In general, for i^{th} gas having partial pressure p_i and mole fraction x_i, we have

$$p_i = x_i \, p_{total}$$

Thus, if total pressure of a mixture of gases is known,then the above equation can be used to calculate pressure exerted by individual gases.

Thus, *the partial pressure of gas in the mixture is the product of its mole fraction and total pressure of the mixture.*

Application of Dalton's law. This law is useful in calculating the pressure of the gases collected over water in the laboratory. The mixture of gas and water vapour has a total pressure equal to atmospheric pressure when the water level is same inside and outside the vessel. For example, oxygen gas is collected over water as shown in Fig. 19. When the water level inside the container becomes equal to outside level, then,

$$p_{atm} = p_{total} \quad \text{(equal to pressure of gas and water vapours)}$$

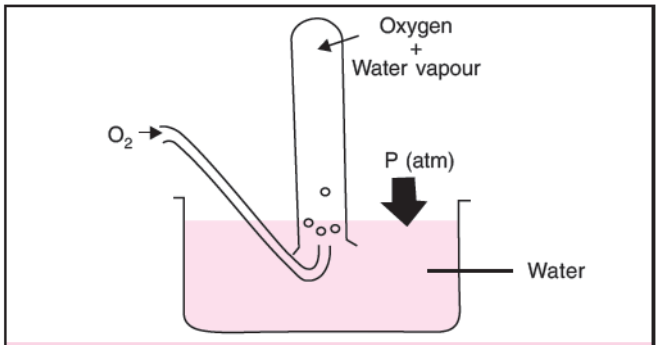

Fig. 19. The collection of oxygen gas over water.

$$= p_{O_2} + p_{H_2O}$$

$$\therefore \quad p_{O_2} = p_{atm} - p_{H_2O}$$

Here p_{H_2O} is the pressure due to water vapours (commonly called **aqueous tension**). Since aqueous tension at different temperatures is known, pressure of dry gas can be easily calculated.

The aqueous tension of water at different temperature is given in Table 5.

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Table 5. Aqueous tension (vapour pressure) of water as a function of temperature.

Temperature (K)	Aqueous tension (bar)
273.15	0.0060
283.15	0.0121
288.15	0.0168
291.15	0.0204
293.15	0.0230
295.15	0.0260
297.15	0.0295
298.15	0.0318
301.15	0.0372
303.15	0.0418

SOLVED EXAMPLES

Example 29.

What will be the pressure of the gas mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of oxygen at 0.7 bar are introduced in a 1 L vessel at 27°C ?

N.C.E.R.T.

Solution: Partial pressure of hydrogen gas

$V_1 = 0.5$ L $\quad V_2 = 1$ L

$p_1 = 0.8$ bar $\quad p_2 = ?$

Applying Boyle's law (constant T and n)

$$p_1V_1 = p_2V_2 \text{ or } \quad p_2 = \frac{p_1V_1}{V_2}$$

$$\therefore \quad p_2 = \frac{(0.8 \text{ bar}) \times (0.5 \text{ L})}{1 \text{ L}}$$

$$= 0.40 \text{ bar}$$

Partial pressure of oxygen gas,

$V_1 = 2.0$ L, $\quad V_2 = 1.0$ L

$p_1 = 0.7$ bar $\quad p_2 = ?$

$$\text{or} \quad p_2 = \frac{p_1V_1}{V_2} = \frac{(0.7 \text{ bar}) \times (2.0 \text{ L})}{(1.0 \text{ L})} = 1.40 \text{ bar}$$

Pressure of the gas mixture,

$$p_{mix} = p_{H_2} + p_{O_2}$$

$$= 0.40 + 1.40 = \textbf{1.80 bar.}$$

Example 30.

Calculate the total pressure in a mixture of 8 g of oxygen and 4 g of hydrogen confined in a vessel of 1 dm^3 at 27°C (R = 0.083 bar dm^3 K^{-1} mol^{-1}).

N.C.E.R.T.

Solution: Partial pressure of oxygen gas,

$$p = \frac{nRT}{V}$$

$n = \frac{8}{32}$ mol, $\quad V = 1 \text{ dm}^3$, T = 300 K

$$p_{(O_2)} = \frac{8 \times 0.083 \times 300}{32 \times 1}$$

$$= 6.225 \text{ bar}$$

Partial pressure of hydrogen gas

$$p = \frac{nRT}{V}$$

$$n = \frac{4}{2} = 2 \text{ mol}$$

$$p(H_2) = \frac{2 \times 0.083 \times 300}{1}$$

$$= 49.8 \text{ bar}$$

Total pressure $= p_{(O_2)} + p_{(H_2)}$

$= 6.225 + 49.8 = \textbf{56.025 bar.}$

Example 31.

A neon-dioxygen mixture contains 70.6g of dioxygen and 167.5 g of neon. If pressure of the mixture of gases in the cylinder is 25 bar, what is the partial pressure of dioxygen and neon in the mixture.

N.C.E.R.T.

Solution: No. of moles of dioxygen $= \frac{70.6}{32}$

$= 2.21$ mol

No. of moles of neon $= \frac{167.5}{20}$

$= 8.375$ mol

Mole fraction of dioxygen, $x_{O_2} = \frac{2.21}{2.21 + 8.375}$

$= 0.21$

Mole fraction of neon, $x_{Ne} = \frac{8.375}{2.29 + 8.375}$

$= 0.79$

Now partial pressure of a gas = mole fraction × total pressure

$\therefore$ Partial pressure of oxygen = 0.21 × (25 bar)

$= \textbf{5.25 bar}$

Partial pressure of neon = 0.79 × (25 bar)

$= \textbf{19.75 bar.}$

Example 32.

A gaseous mixture containing 50 g of nitrogen and 10 g of oxygen were enclosed in a vessel of 10L capacity at 27°C. Calculate

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(a) the number of moles of each gas.
(b) the partial pressure of each gas.
(c) the total pressure of gaseous mixture.

Solution: Volume of vessel = 10 L

Temperature = 27 + 273 = 300 K

Step I. *To calculate the moles of each gas.*

Weight of nitrogen = 50 g

Molar mass of nitrogen = 28

$$\text{Moles of nitrogen} = \frac{50}{28} = \mathbf{1.79}$$

Weight of oxygen = 10 g

Molar mass of oxygen = 32

$$\text{Moles of oxygen} = \frac{10}{32} = \mathbf{0.31}$$

Step II. *To calculate the partial pressure of each gas.*

According to general gas equation

$$pV = nRT \quad \text{or} \quad p = \frac{nRT}{V}$$

∴ Partial pressure of nitrogen,

$$p_{N_2} = \frac{1.79 \times 0.082 \times 300}{10} = \mathbf{4.40\ atm.}$$

Partial pressure of oxygen,

$$p_{O_2} = \frac{0.31 \times 0.082 \times 300}{10} = \mathbf{0.76\ atm.}$$

Step III. *To calculate the total pressure.*

According to Dalton's law of partial pressures, the total pressure of the gaseous mixture :

$$p = p_{N_2} + p_{O_2}$$

$$= 4.40 + 0.76 = \mathbf{5.16\ atm.}$$

❑ Example 33.

135 mL of a gas is collected over water at 25°C and 0.993 bar. If the gas weighs 0.160 g and the aqueous tension at 25°C is 0.0317, calculate the molar mass of the gas.

Solution: $p_{gas} = p_{total} - p_{H_2O}$

$p_{total} = 0.993$ bar, $pH_2O = 0.0317$ bar

∴ $p_{gas} = 0.993 - 0.0317 = 0.9613$ bar

Now $pV = nRT$

But $n = \frac{m}{M}$, $pV = \frac{m}{M}RT$ or $M = \frac{mRT}{pV}$

$m = 0.160$ g, $V = 135$ mL $= \frac{135}{1000} = 0.135$ dm^3

$T = 25 + 273 = 298$ K, $p = 0.9613$ bar

$R = 0.083$ bar dm^3 mol^{-1} K^{-1}

Substituting the values,

$$M = \frac{(0.160\text{ g}) \times (0.083\text{ bar dm}^3\text{ mol}^{-1}\text{ K}^{-1}) \times (298\text{ K})}{(0.9613\text{ bar}) \times (0.135\text{ dm}^3)}$$

$$= \mathbf{30.49\ g\ mol^{-1}}$$

Practice Problems

26. 500 mL of nitrogen at 0.936 bar pressure and 1000 mL oxygen at 0.80 bar pressure are put together in a 2 L flask. If temperature is kept constant, calculate the final pressure of the mixture.

27. 400 mL of oxygen are collected over water at 25°C and 0.948 bar pressure. Find the volume of dry gas at S.T.P. (Aqueous tension at 25°C = 0.0318 bar).

28. A 2.5 L flask contains 0.25 mol each of sulphur dioxide and nitrogen gas at 27°C. Calculate the partial pressure of each gas and also the total pressure.

29. A 5.0 L flask contains 19.5 g of SO_3 and 1.0 g of He gas at 20°C. Calculate the partial pressures exerted by SO_3 and He and the total pressure of the gaseous mixture.

30. 1.00 mol of N_2 and 3.00 mol of H_2 are present in a container of volume 10.0 dm^3 at 298 K. What is the total pressure of the mixture ?

31. What will be the pressure exerted by a mixture of 3.2 g of methane (CH_4) and 4.4 g of carbon dioxide (CO_2) in a 9 dm^3 flask at 27°C. ***N.C.E.R.T.***

32. The composition of dry air at sea level is approximately :

$N_2 = 75.5$, $O_2 = 23.2$, Ar = 1.3 in percentage by mass. What is the partial pressure of each component when the total pressure is 1.0 bar ?

33. A 1.0 L flask contains 2.0 g of N_2, 0.4 g H_2 and 9.0 of O_2 at 27°C. What is the pressure in the flask ?

34. 0.6 g of a gas at 15°C and 745 mm Hg occupies 200 cm^3. It occupies 182.6 cm^3 in dry state at N.T.P. Calculate the aqueous tension at 15°C.

35. A mixture of hydrogen and oxygen in one bar pressure contains 20% by weight of hydrogen Calculate the partial pressure of hydrogen. ***N.C.E.R.T.***

Answers to Practice Problems

26. 0.634 bar

27. 335.7 mL

28. 4.98×10^5 Pa

29. 2.37 atm

30. 9.91 bar

31. 8.31×10^4 Pa

32. $p(N_2) = 0.781$ bar
$p(O_2) = 0.210$ bar
$p(Ar) = 0.009$ bar

33. 13.62 atm

34. 13 mm Hg

35. 0.8 bar

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7. Graham's Law of Diffusion or Effusion*

It is commonly observed that if a bottle of ammonia is opened in one corner of the laboratory, its smell can be felt in other corner of the laboratory after some time. The actual spreading of gases can be seen if a cylinder of colourless hydrogen gas is inverted over a cylinder of brown bromine vapour. Let two gases be separated in the beginning by a disc in between the cylinders. When the disc is removed, it is found that both the cylinders become yellowish brown (Fig. 20). This means that hydrogen has travelled from upper to lower cylinder and bromine has moved from lower to upper cylinder.

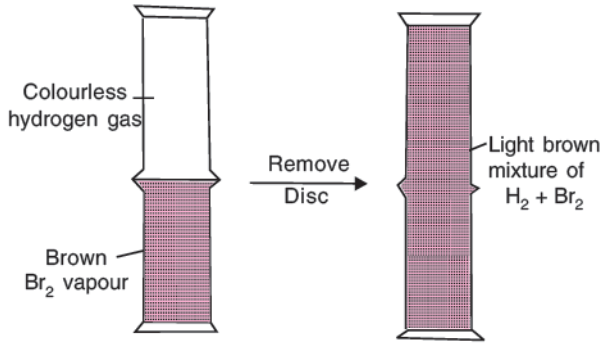

Fig. 20. Diffusion of gases.

This shows that the gases have the tendency to intermix and spread throughout the available space. This property is known as *diffusion*. Thus, **diffusion** is defined as ***spreading of molecules of a gas throughout the available space.***

The diffusion of gases is due to *rapid movement of gas molecules and the presence of large empty space between the molecules*. When the two gases are brought in contact, the molecules of one gas, being in motion go in between empty spaces of the other gas. They move from a region of higher concentration to that of lower concentration till the concentration of mixture becomes uniform throughout.

Graham's Law of Diffusion

Graham studied the rates of diffusion of different gases and gave a law known as **Graham's law of diffusion.** This states that

under similar conditions of temperature and pressure, the rates of diffusion of gases are inversely proportional to the square roots of their densities.

That is,

$$\text{Rate of diffusion } \alpha \sqrt{\frac{1}{\text{Density}}}$$

Let r_1, and r_2, be the rates of diffusion of two gases A and B and d_1 and d_2 be their densities respectively. Then, according to Graham's law of diffusion,

$$r_1 \propto \sqrt{\frac{1}{d_1}} \quad \text{and} \quad r_2 \propto \sqrt{\frac{1}{d_2}}$$

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad \text{(same T and P)}$$

This is the *mathematical expression for Graham's law.*

Now, we know that molecular mass is twice the vapour density. Therefore, the above expression may be written as :

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2/2}{M_1/2}} = \sqrt{\frac{M_2}{M_1}}$$

where M_1 and M_2 are the molecular masses of the gases having densities d_1 and d_2 respectively. Thus, Graham's law may be also be stated as :

under similar conditions of temperature and pressure, the rates of diffusion of gases are inversely proportional to the square roots of their molecular masses.

Again, rate of diffusion of a gas is equal to the volume of the gas which diffuses per unit time, *i.e.*,

$$\text{Rate of diffusion} = \frac{\text{Volume of the gas diffused}}{\text{Time take for diffusion}}$$

$$\text{or} \qquad r = \frac{V}{t}$$

If V_1 and V_2 are the volumes of the gases diffusing in time t_1 and t_2 respectively, then

$$r_1 = \frac{V_1}{t_1} \text{ and } r_2 = \frac{V_2}{t_2}$$

$$\text{Therefore, } \frac{r_1}{r_2} = \frac{V_1/t_1}{V_2/t_2} = \sqrt{\frac{d_2}{d_1}}$$

- If the two gases diffused in the same time, *i.e,* $t_1 = t_2$

$$\text{then} \qquad \frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

- If the volume diffused is the same, *i.e.,* $V_1 = V_2$

$$\text{then} \qquad \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

If two gases are taken at different pressures, then larger the pressure, larger is the number of molecules hitting per unit area and therefore, larger is the rate of diffusion. In such cases, Graham's law of diffusion can be written as :

$$\frac{r_1}{r_2} = \frac{p_1}{p_2}\sqrt{\frac{d_2}{d_1}} \quad \text{or} \quad = \frac{p_1}{p_2}\sqrt{\frac{M_2}{M_1}}$$

*This is not included in the CBSE syllabus but required for competitive examinations.

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Similarly, for two gases undergoing diffusion at the same pressure but at two different temperatures,

$$\frac{r_1}{r_2} = \sqrt{\frac{T_1\, d_2}{T_2\, d_1}} \quad \text{or} \quad = \sqrt{\frac{T_1 M_2}{T_2 M_1}}$$

Effusion

It is a particular case of diffusion in which the gases contained in a vessel are allowed to escape through a small aperture (hole). The Graham's law of diffusion is also valid for effusion.

The process of diffusion and effusion are shown below :

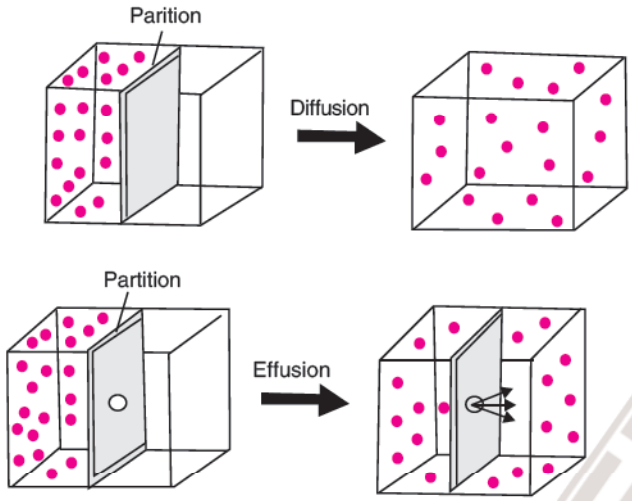

Fig. 21. Processes of diffusion and effusion.

In diffusion, when partition is removed, the molecules spread out and fill the whole container. On the other hand, in effusion the particles escape from a very small hole in the partition.

❑ Example 34.

An unknown gas diffuses four times as quickly as oxygen. Calculate the molar mass of the gas.

Solution: Let the rate of diffusion of oxygen,

$$r\,(O_2) = r_1$$

Then rate of diffusion of unknown gas,

$$r\,(x) = 4r_1$$

Molar mass of O_2, $M\,(O_2) = 32$

Molar mass of unknown gas $M\,(x) = M$

From Graham's law of diffusion, $\frac{r(O_2)}{r(x)} = \sqrt{\frac{M(x)}{M(O_2)}}$

or $\frac{r_1}{4r_1} = \sqrt{\frac{M(x)}{32}}$

Squaring both sides, $\frac{1}{16} = \frac{M(x)}{32}$

or $M(x) = \frac{32}{16} = 2$

Hence, molar mass of unknown gas **= 2 a.m.u.**

❑ Example 35.

Relative densities of carbon dioxide and oxygen are 22 and 16 respectively. If 25 cc of carbon dioxide diffuses in 75 seconds, what volume of oxygen will diffuses in 96 seconds under similar conditions ?

Solution:

Here, volume of carbon dioxide, $V(CO_2) = 25$ cc

Time taken, $t(CO_2) = 75$ seconds

Let the volume of oxygen diffused, $V(O_2) = V$ cc

Time taken, $t(O_2) = 96$ seconds

Relative density of carbon dioxide, $d(CO_2) = 22$

Relative density of oxygen, $d(O_2) = 16$

Now $\frac{r(O_2)}{r(CO_2)} = \sqrt{\frac{d\,(CO_2)}{d\,(O_2)}}$

or $\frac{V(O_2)}{t(O_2)} \Big/ \frac{V(CO_2)}{t(CO_2)} = \sqrt{\frac{22}{16}}$

or $\frac{V(O_2)}{t(O_2)} \times \frac{t(CO_2)}{V(CO_2)} = \sqrt{\frac{22}{16}}$

or $\frac{V(O_2) \times 75}{96 \times 25} = \sqrt{\frac{22}{16}} = 1.172$

or $V(O_2) = \frac{1.172 \times 96 \times 25}{75} = \mathbf{37.5\ cc}$

Thus, volume of oxygen diffused = **37.5 cc.**

❑ Example 36.

For 10 minutes each, at 27°C, from two identical holes nitrogen and an unkown gas are leaked into a common vessel of 3L capacity. The resulting pressure is 4.18 bar and its mixture contains 0.4 mole of nitrogen. What is the molar mass of unkown gas ?

Solution: Let us calculate the total number of moles in the mixture

$$pV = nRT \quad \text{or} \quad n = \frac{pV}{RT}$$

$p = 4.18$ bar, $V = 3$ L, $T = 300$ K,

$R = 0.083$ bar L mol^{-1} K^{-1}

$$\therefore \quad n = \frac{4.18 \times 3}{0.083 \times 300} = 0.504 \text{ mol}$$

Moles of N_2 present in the mixture = 0.4 mol

Moles of unkown gas diffused in the same time

$= 0.504 - 0.4 = 0.104$ mol

This means that in 10 min (same time), 0.4 mol of N_2 and 0.104 mol of unkown gas diffuse out.

As volumes under similar conditions are directly proportional to their number of moles, applying Graham's law of diffusion :

$$\frac{r_{N_2}}{r_X} = \sqrt{\frac{M_X}{M_{N_2}}}$$

$$\frac{\frac{0.4}{10}}{\frac{0.104}{10}} = \sqrt{\frac{M_X}{28}}$$

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$$\therefore \quad \frac{0.4}{0.104} = \sqrt{\frac{M_X}{28}}$$

$$\text{or} \quad 14.8 = \frac{M_X}{28}$$

$$\text{or} \quad M_X = 14.8 \times 28 = \mathbf{414.4\ g\ mol^{-1}}.$$

❑ **Example 37.**

A 4 : 1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. What is the composition of the mixture effusing out initially ?

Solution: The molar ratio of He : CH_4 = 4 : 1

$$\text{Partial pressure of He} = \frac{4}{4+1} \times 20 = 16 \text{ bar}$$

$$\text{Partial pressure of } CH_4 = \frac{1}{4+1} \times 20 = 4 \text{ bar}$$

$$\text{Now,} \quad \frac{V_{He}}{V_{CH_4}} = \frac{p_{He}}{p_{CH_4}} \times \sqrt{\frac{M_{CH_4}}{M_{He}}}$$

Since time of effusion is same,

$$\frac{r_{He}}{r_{CH_4}} = \frac{p_{He}}{p_{CH_4}} \times \sqrt{\frac{M_{CH_4}}{M_{He}}}$$

$$= \frac{16}{4} \times \sqrt{\frac{16}{4}} = 8$$

∴ Molar ratio of mixture initially effusing out is

$$He : CH_4 = 8 : 1.$$

❑ **Example 38.**

One mole of nitrogen gas at 0.8 atm takes 38s to diffuse through a pin hole, whereas one mole of an unkown compound of Xe with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Calculate the molecular formula of the compound.

Solution: Rate of diffusion $\propto \frac{p}{\sqrt{M}}$

$$\text{or} \quad \frac{r_2}{r_1} = \frac{p_2}{p_1}\sqrt{\frac{M_1}{M_2}}$$

Since r is $\propto \frac{1}{t}$, we may write,

$$\frac{t_1}{t_2} = \frac{p_2}{p_1}\sqrt{\frac{M_1}{M_2}}$$

$$\text{or} \quad \frac{t_{N_2}}{t_g} = \frac{p_g}{p_{N_2}} \times \sqrt{\frac{M_{N_2}}{M_g}}$$

$$\frac{38}{57} = \frac{1.6}{0.8} \times \sqrt{\frac{28}{M_g}}$$

$$\therefore \quad M_g = \left(\frac{1.6}{0.8} \times \frac{57}{38}\right)^2 \times 28 = 252$$

Let the molecular formula of compound be $\mathbf{XeF_n}$

$$M_{Xe} + nM_F = 252$$

(At. mass of Xe = 131u, At. mass of F = 19u)

$$131 + n \times 19 = 252$$

$$19n = 252 - 131 = 121$$

$$\therefore \quad n = \frac{121}{19} = 6.3 \text{ or } 6$$

Molecular formula = $\mathbf{XeF_6}$.

❑ **Example 39.**

A straight glass tube has two inlets X and Y at the two ends. The length of the tube is 200 cm. HCl gas through inlet X and NH_3 gas through inlet Y are allowed to enter the tube at the same time. White fumes first appear at a point P inside the tube. Find the distance of P from X.

Solution: According to Graham's law of diffusion,

$$\frac{\text{Rate of diffusion of HCl}}{\text{Rate of diffusion of } NH_3} = \sqrt{\frac{\text{Molar mass of } NH_3}{\text{Molar mass of HCl}}}$$

Molar mass of NH_3 = 17,

Molar mass of HCl = 36.5

Let the distance between P and X = d cm

∴ Distance between P and Y = $(200 - d)$ cm.

Let they meet at P in time t.

$$\text{Rate of diffusion of HCl} = \frac{d}{t}$$

$$\text{Rate of diffusion of } NH_3 = \frac{200 - d}{t}$$

$$\therefore \quad \frac{d/t}{(200-d)/t} = \sqrt{\frac{17}{36.5}}$$

$$\frac{d}{200-d} = 0.6824$$

$$d = (200 - d)(0.6824)$$

$$\text{or} \quad d + 0.6824\, d = 200 \times 0.6824$$

$$\text{or} \quad d = \frac{200 \times 0.6824}{1.6824}$$

$$= \mathbf{81.12\ cm.}$$

Importance of Graham's law

The Graham's law has the following important applications :

(*i*) It helps in separation of gases having different densities by diffusion.

(*ii*) It is helpful in determining the densities and molecular masses of unknown gases by comparing their rates of diffusion with known gases.

(*iii*) It helps in separating the isotopes of some elements.

Practice Problems

36. Compare the rates of diffusion of $^{235}UF_6$ and $^{238U}F_6$.

37. The volume of a gas X and chlorine diffusing during the same time are 35 ml and 29 ml respectively. If the molar mass of chlorine is 71, calculate the molar mass of gas (X).

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38. A certain gas, G takes four times as long to effuse out as H_2. What is its molecular mass ?

39. Equal volumes of two gases A and B diffuse through a porous pot in 20 and 10 seconds respectively. If the molar mass of A be 80, find the molar mass of B.

40. Which of the two gases : ammonia or hydrogen chloride will diffuse faster and by what factor ?

41. 180 cm^3 of a hydrocarbon diffuses in 15 min, while under the same conditions, 120 cm^3 of sulphur dioxide diffuse in 20 min. If the molecular mass of SO_2 is 64, what is the molecular formula of the hydrocarbon ?

42. A gaseous mixture of O_2 and an unknown gas 'X' containing 20 mole % of X diffused through a small hole in 245 seconds while O_2 takes 220 seconds to diffuse through the same hole under similar conditions. Calculate the molecular mass of X.

43. Calculate the molecular mass of gas A which diffuses four times as fast as another gas B which diffuses twice as fast as another gas C. Molecular mass of C is 128.

Answers to Practice Problems

36. 1.004:1 **37.** 48.75 **38.** 32
39. 20 g mol^{-1} **40.** NH_3, 1.46 times
41. CH_4 **42.** 70.4 **43.** 2 g mol^{-1}

Hints & Solutions on page 58

Advanced Level PROBLEMS *Accelerate Your Potential (for JEE Advance)*

Problem 1. A perfectly elastic spherical balloon of 0.2 diameter was filled with hydrogen gas at sea level where atmospheric pressure is 1 atm. What will be its diameter when it has risen to an altitude where the pressure is 0.65 atm? (Assume no change in temperature and atmospheric pressure at sea level).

Solution The volume of spherical balloon of radius r,

$$V = \frac{4}{3}\pi r^3$$

At sea level, volume $V_1 = \frac{4}{3}\pi r_1^3$

(r_1 is the radius of balloon at sea level)

$$r_1 = \frac{0.2}{2}\text{ m} = 0.1\text{ m}$$

$$V_1 = \frac{4}{3}\pi (0.1\text{ m})^3$$

Pressure at sea level, p_1 = 1 atm.

Volume at altitude, $V_2 = \frac{4}{3}\pi r_2^3$

(r_2 is the radius of balloon altitude)

Pressure at the altitude = 0.65 atm.

According to Boyle's law (since temperature is constant)

$$p_1V_1 = p_2V_2 \quad \text{or} \quad V_2 = \frac{p_1V_1}{p_2}$$

or $$\frac{4}{3}\pi r_2^3 = \frac{(1\text{ atm}) \times \frac{4}{3}\pi (0.1\text{ m})^3}{0.65\text{ atm}}$$

$$r_2^3 = \frac{1 \times (0.1)^3}{0.65}$$

$$= 1.54 \times 10^{-3}\text{ m}^3$$

or $$r_2 = (1.54 \times 10^{-3}\text{ m}^3)^{1/3}$$

$$= \mathbf{0.1154\text{ m}}$$

$\therefore$ Diameter of the balloon at the altitude $= 2 \times 0.1154$

$$= \mathbf{0.2308\text{ m}}.$$

Problem 2. A 2.0 L container at 25°C contain 1.25 mol of O_2 and 3.2 mol of C.

***(a)* What is the initial pressure in the flask ?**

***(b)* If the carbon and oxygen react as completely as possible to form CO, what will be the final pressure in the container ?**

Solution The container contains 1.25 mol of O_2 and 3.2 mol of C. Since only oxygen is gaseous and carbon will not exert any pressure.

$$n = 1.25\text{ mol}, V = 2.0\text{ L}, T = 273 + 25 = 298\text{ K}$$

$$\therefore \quad p = \frac{nRT}{V}$$

$$= \frac{(1.25\text{ mol}) \times (0.0821\text{ L atm mol}^{-1}\text{K}^{-1})(298\text{ K})}{(2.0\text{ L})}$$

$$= 15.3\text{ atm}$$

(*b*) The reaction is

$$C + \frac{1}{2}O_2 \longrightarrow CO$$

According to the equation, 1 mol of CO will be produced for every $\frac{1}{2}$ mol of O_2 used.

$\frac{1}{2}$ mole of O_2 gives CO = 1 mole

1.25 mole of O_2 will give CO = $1 \times 2 \times 1.25$

$$= 2.50\text{ mol}$$

The final pressure is

$$p = \frac{(2.50\text{ mol}) \times (0.0821\text{ L atm K}^{-1}\text{ mol}^{-1}) \times (298\text{ K})}{2.0\text{ L}}$$

$$= \mathbf{30.6\text{ atm}}.$$

Problem 3. A spherical balloon of 21 cm diameter is to be filled with hydrogen at N.T.P. from a cylinder containing the gas at 20 atmosphere and 27°C. If the cylinder can hold 2.82 litres of water, calculate the number of balloons that can be filled up.

Solution Volume of balloon, $V = \frac{4}{3}\pi r^3$.

$$r = \frac{21}{2}\text{ cm}$$

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$$V = \frac{4}{3} \times \frac{22}{7} \times \left(\frac{21}{2}\right)^3$$

$$= \mathbf{4851\ mL.}$$

Volume of hydrogen in the cylinder at N.T.P. can be calcualted as :

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

Volume of the cylinder = 2.82 L = 2820 mL

p_1 = 20 atm $\quad$ p_2 = 1 atm

V_1 = 2820 L $\quad$ V_2 = ?

T_1 = 273 + 27 = 300 K $\quad$ T_2 = 273

$$V_2 = \frac{p_1V_1T_2}{p_2T_1}$$

$$= \frac{20 \times 2820 \times 273}{1 \times 300} = 51324\ \text{mL.}$$

When the pressure in the cylinder is reduced to 1 atm, no more H_2 will be released and hence 2820 mL of H_2 will be left in the cylinder.

∴ Vol. of hydrogen available for filling balloons

= 51324 – 2820 = 48504 ml

No. of balloons to be filled = $\frac{48504}{4851}$ **= 10.**

Problem 4. An evacuated bulb of unknown volume is filled with H_2 gas at room temperature (30°C). The pressure of the gas in the bulb is 750 mm Hg. A portion of the gas is transferred to a different flask and found to occupy a volume of 50.0 mL at 1 atm pressure and at the same temperature. The pressure of the H_2 gas remaining in the original bulb drops to 600 mm Hg. What is the volume of the bulb assuming H_2 gas is an ideal gas?

Solution Let volume of the bulb = V

$$p = 750\ \text{mm Hg} = \frac{750}{760}\text{atm}$$

Initial moles of H_2 $(n_1) = \frac{pV}{RT} = \frac{750 \times V}{760 \times 82.1 \times 303}$

Moles transferred $(n_2) = \frac{760 \times 50}{760 \times 82.1 \times 303}$

Moles of H_2 left in the bulb = $n_1 - n_2$

$p(H_2)$ left in bulb = $\frac{600}{760}$atm

Using ideal gas equation,

$$pV = nRT$$

$$\frac{600}{760} \times V = (n_1 - n_2) \times 82.1 \times 303$$

$$\frac{600}{760} \times V = \left(\frac{750 \times V}{760 \times 82.1 \times 303} - \frac{760 \times 50}{760 \times 82.1 \times 303}\right) \times 82.1 \times 303$$

$$\frac{600}{760} \times V = \left(\frac{750 \times V}{760} - \frac{760}{760} \times 50\right)$$

or $$\frac{600}{760}V - \frac{750}{760}V = -50$$

$$\frac{150}{760} \times V = 50$$

or $$V = \mathbf{253.3\ mL}$$

Problem 5. A 10 dm^3 flask at 298 K contains a gaseous mixture of CO and CO_2 at a total pressure of 2.0 bar. If 0.20 mole of CO is present, find its partial pressure and also that of CO_2.

Solution According to Dalton's law of partial pressure

$$p_{total} = p_{(CO)} + p_{(CO_2)} = 2.0\ \text{bar}$$

Partial pressure of CO, $p_{(CO)} = \frac{n(CO)RT}{V}$

$$= \frac{(0.2\ \text{mol}) \times (0.083\ \text{bar dm}^3\ \text{K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})}{10\ \text{dm}^3}$$

= 0.495 bar.

Partial pressure of CO_2,

$$p_{(CO_2)} = p_{total} - p_{(CO)}$$

$$= 2.0 - 0.495 = \mathbf{1.505\ bar.}$$

Problem 6. The circulation of blood in the human body supplied oxygen and removes carbon dioxide. The concentration of oxygen and carbon dioxide is variable but on an average 100 ml of blood contains 0.02 g of oxygen and 0.08 g of carbon dioxide. Calculate the volume of oxygen and carbon dioxide at 1 atm and body temperature (37°C) assuming that there are 10 litres of blood in the human body.

Solution Volume of blood in human body = 10 L

= 10 × 1000 mL

Wt. of oxygen in blood = $\frac{0.02 \times 10 \times 1000}{100} = 2$ g

Wt. of carbon dioxide in blood = $\frac{0.08 \times 10 \times 1000}{100} = 8$ g

Now, $$pV = nRT \text{ or } V = \frac{nRT}{p}$$

p = 1 atm,

R = 0.0821 L atm mol^{-1} K^{-1},

T = 273 + 37 = 310 K

For oxygen, $n = \frac{2}{32}$ mol

$$\therefore \quad V = \frac{2}{32} \times \frac{0.0821 \times 310}{1} = 1.59\ \text{L}$$

For carbon dioxide, $n = \frac{8}{44}$ mol

$$\therefore\ V = \frac{8}{44} \times \frac{0.0821 \times 310}{1} = 4.62\ \text{L.}$$

Problem 7. An open vessel at 27°C is heated unitil three-fifth of the air in it has been expelled. Assuming volume of the vessel constant, find the temperature to which the vessel has been heated.

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Solution Since the vessel is open, its pressure will remain constant.

Let the number of moles of air at 27°C = n

No. of moles of air left after heating = $n - \frac{3}{5}n = \frac{2}{5}n$

Now $pV = nRT$

At 27°C $pV = nR \times 300$ ...(*i*)

At higher temperature, T(K)

$$pV = \frac{2}{5}nRT$$

Since pV is constant,

or $nR \times 300 = \frac{2}{5}nRT$ ...(*ii*)

$$T = \frac{300 \times 5}{2} = 750 \text{ K}$$

or $T = 750 - 273$

$= 477°C.$

Problem 8. An LPG (Liquefied Petroleum Gas) cylinder weighs 14.8 kg when empty. When full, it weighs 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27°C, the mass of the full cylinder is reduced to 23.2 kg. Find out the volume of the gas in cubic metres used up at the normal usage conditions, and the final pressure inside the cylinder. Assume LPG to be n-butane with normal boiling point of 0°C.

Solution Weight of LPG originally present

$= 29.0 - 14.8$

$= 14.2$ kg

Pressure = 2.5 atm

Weight of L.P.G. present after use = $23.2 - 14.8$

$= 8.4$ kg

Since volume of the cylinder is constant, applying

$$pV = nRT$$

$$\frac{p_1}{p_2} = \frac{n_1}{n_2} = \frac{W_1/M}{W_2/M} = \frac{W_1}{W_2}$$

$$\frac{2.5}{p_2} = \frac{14.2}{8.4}$$

$$p_2 = \frac{2.5 \times 8.4}{14.2} = 1.48 \text{ atm}$$

or Weight of used gas = $14.2 - 8.4 = 5.8$ kg

$$\text{Moles of gas} = \frac{5.8 \times 10^3}{58} = 100 \text{ moles}$$

Normal conditions

$p = 1$ atm;

$T = 273 + 27 = 300$

Volume of 100 mL of LPG at 1 atm and 300 K

$$V = \frac{nRT}{p}$$

$$= \frac{100 \times 0.082 \times 300}{1} = 2463 \text{ litre}$$

$V = \mathbf{2.463\ m^3}$.

Problem 9. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 26.7°C. Calculate the number of moles of NO_2 in 100 g mixture.

Solution Molecular weight of mixture

$= 2 \times$ Vapour density

$= 2 \times 38.3 = 76.6$

Let the mixture contains x g of NO_2 and $(100–x)$ g of N_2O_4

$$\text{Moles of } NO_2 = \frac{x}{46}$$

$$\text{Moles of } N_2O_4 = \frac{100 - x}{92}$$

$$\text{Moles of mixture} = \frac{100}{76.6}$$

Now, moles of NO_2 and N_2O_4 = Moles of mixture

$$\frac{x}{46} + \frac{100 - x}{92} = \frac{100}{76.6}$$

$$2x + 100 - x = \frac{100 \times 92}{76.6}$$

$$100 + x = 120.1$$

$\therefore$ $x = 120.1 - 100 = 20.1$

$\therefore$ $$\text{Moles of } NO_2 = \frac{20.1}{46} = 0.437$$

Problem 10. The pressure exerted by 12 g of an ideal gas at temperature t°C in a vessel of volume V litre is one atm. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V (Molecular mass of gas = 120).

Solution Moles of gas = $\frac{12}{120} = 0.1$ mol

$p = 1$ atm, $T = t°C = (273 + t)$ K, Volume = V

According to ideal gas equation,

$$pV = nRT$$

$\therefore$ $1 \times V = 0.1 \times R \times (273 + t)$ ...(*i*)

Now, $p = 1 + \frac{10}{100} = 1.1$ atm, $T = t + 273 + 10$

$= 283 + t$ K

Volume = V (same)

$\therefore$ $1.1 \times V = 0.1 \times R \times (283 + t)$ ...(*ii*)

Dividing Eq. (*ii*) by (*i*), we have

$$\frac{1.1}{1} = \frac{283 + t}{273 + t}$$

$$283 + t = 1.1(273 + t) = 308.3 + 1.1t$$

or $-0.1t = 17.3$

or $t = -173°C$

Substituting the value of t in equation (*i*):

$1 \times V = 0.1 \times 0.082 \times (273 - 173)$

or $V = 0.1 \times 0.082 \times 100$

$= \mathbf{0.82\ L}$.

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KINETIC MOLECULAR THEORY OF GASES

The various gas laws discussed earlier were merely based upon experimental observations. There was no theoretical background to explain them. In order to account for the observed behaviour of gases, a model was proposed which takes into account *molecular concept* as well as the *kinetic concept* of gas molecules. This model was known as **kinetic molecular theory of gases**. It is also known as microscopic model because its assumptions relate to microscopic particles (atoms or molecules) present in gases. The theory was put forward by Bernoulli and was further developed and extended by Clausius, Maxwell, Boltzmann and others. The main postulates of this theory are given below :

Postulates of Kinetic Molecular Theory

The important postulates of the theory are :

(*i*) *All gases are made up of a very large number of extremely small identical particles (atoms or molecules).*

(*ii*) *The molecules are separated from one another by large distances. The empty spaces among the molecules are so large that the actual volume of the molecules is negligible as compared to the total volume of the gas.*

(*iii*) *The molecules are in a state of ceaseless and random motion in all the directions. During their motion, they keep on colliding with one another and also with the walls of the container and thus, change their directions.*

(*iv*) *Molecular collisions are perfectly elastic, i.e. no loss of energy occurs when the molecules collide with one another or with the walls of the container. However, there may be redistribution of energy during the collisions.*

(*v*) *There are no forces of interaction (attractive or repulsive) between molecules at ordinary temperature and pressure. They move completely independent of one another.*

(*vi*) *The pressure exerted by the gas is due to the collision of its molecules on the walls of the container.*

(*vii*) *The average kinetic energy of the gas molecules is directly proportional to the absolute temperature.*

Justification for the postulates

The above postulates of kinetic molecular theory of gases have the following justifications :

(*i*) The first postulate is in accordance with the general particle or molecular nature of matter.

(*ii*) It is well known fact that the gases are highly compressible and they also have the tendency to expand indefinitely. These facts clearly support the second postulate. When pressure is applied, the intermolecular distance decreases, and as a result the volume of the gas decreases. Further, the volume occupied by the molecules is so small that it may be neglected in comparison to the total volume. For example, it has been experimentally observed that the molecules of gases like H_2 or N_2 or O_2 have volume less than 0.1% of the total volume of the gas.

(*iii*) It is a common observation that smoke or dust particles in the air are in constant zig-zag motion. Smoke or dust represents solid particles suspended in air which is a mixture of different gases. These particles are colliding with the molecules of the gases and their zig-zag motion clearly shows that the gas molecules, too, have identical motion. If the particles were at rest and occupied fixed positions, then the gas would have had a fixed shape. However, this is not observed.

(*iv*) The molecules are constantly moving in all directions. During the course of their motion, they collide with one another and also with the walls of the container. During each collision, the speed and the direction of motion of molecules undergo a change. However, the molecular collisions are perfectly elastic, *i.e.* the total kinetic energy remains constant. In these collisions, energy may be transferred from one molecule to another but the total kinetic energy remains the same. If these collisions are not elastic, there should have been continuous loss of kinetic energy and ultimately, the molecules would stop. But this does not happen.

(*v*) It is a common observation that the gas expands when the pressure on the gas is released. The expansion of gas means the movement of molecules away from one another and increase the voids between them. This is possible if the attractive forces between the molecules are negligible.

(*vi*) When the gas is enclosed in a vessel, its molecules being in rapid motion constantly go on striking the walls. As a result, the walls experience some outward force and this force per unit area is termed as gas pressure.

(*vii*) Due to molecular collisions, the different molecules have different speeds. As a result, the molecules have different kinetic energies (K.E. = $\frac{1}{2} mv^2$). Under these circumstances, it is assumed that the average kinetic energy is directly proportional to the absolute temperature.

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It has been observed that when the gas is heated, its temperature rises. This is because of the fact that thermal energy results into increase in the average kinetic energy of gas molecules. Therefore, these molecules strike the walls of the container more frequently and thus exert more pressure. Therefore, it is seen that on heating a gas at constant volume, the pressure increases.

KINETIC GAS EQUATION

On the basis of postulates of kinetic molecular theory, an equation was derived for the pressure of the gas. The equation is known as **kinetic gas equation** and is given as :

$$pV = \frac{1}{3} m N\overline{u^2} \qquad ...(i)$$

where N is the number of molecules in volume V, m is the mass of a molecule and u is the velocity (known as root mean square velocity) of the molecules.

Average Kinetic Energy of Gas Molecules

Using the above relationship and gas laws, relationship between average translational kinetic energy of a molecule at a temperature T of the gas can be derived.

The average translational kinetic energy of a molecule is $\frac{1}{2} m \bar{u}^2$ at a temperature T of the gas. The total energy of the whole of the gas containing N molecules is

$$E_k = \frac{1}{2} m N\overline{u^2} \qquad ...(ii)$$

The kinetic gas equation is

$$pV = \frac{1}{3} m N\overline{u^2}$$

or $$pV = \frac{2}{3} \cdot \frac{1}{2} m N\overline{u^2}$$

or $$pV = \frac{2}{3} E_k \qquad ...(iii)$$

Comparing this equation with the general gas equation,

$$pV = RT \text{ for one mole of gas}$$

$$\therefore \quad RT = \frac{2}{3} E_k \text{ or } E_k = \frac{3}{2} RT \qquad ...(iv)$$

Similarly, kinetic energy for n moles of the gas

$$E_k = \frac{3}{2} nRT \qquad ...(v)$$

The average kinetic energy per molecule can be obtained by dividing both sides of the above equation by Avogadro number (6.022×10^{23}) of molecules, N_A.

Average kinetic energy for 1 molecule

$$= \frac{3}{2} \frac{RT}{N_A} = \frac{3}{2} k_b T \qquad ...(vi)$$

where $k_b = \frac{R}{N_A}$ and is called **Boltzmann constant.**

Thus, E_k (kinetic energy) $\propto$ T

Hence, average kinetic energy of a gas is directly proportional to its absolute temperature irrespective of its nature. *This is also one of the assumptions of kinetic molecular theory.*

Further, since kinetic energy is directly proportional to root mean square velocity,

$\therefore$ K.E. $\propto u^2$

It follows that $u^2 \propto T$ or $u \propto \sqrt{T}$

Thus, *molecular velocity of any gas is directly proportional to the square root of the absolute temperature.* This molecular motion is quite often termed as **thermal motion** of the molecules. At absolute zero (T = 0), kinetic energy of the gas becomes zero. Thus, the thermal motion of the molecules is expected to cease at this temperature. Since a gas liquefies before this temperature is actually reached, therefore, the molecular motion in the gas does not become zero.

Explanation of Gas Laws on the Basis of Kinetic Molecular Theory of Gases

The various gas laws can be theoretically explained with the help of the basic postulates of kinetic molecular theory. Let us discuss these :

I. Boyle's law. According to kinetic molecular theory, the pressure exerted by a gas is due to striking of the molecules of the gas on the walls of the container [postulate, (*vi*)]. Therefore, it depends upon the number of molecular impacts or collisions per unit area per second on the walls. If the temperature is kept constant, the average speed of the molecules ($\frac{1}{2} mv^2 \propto T$) remains the same. Now, if the volume is increased, there will be less number of molecules hitting each unit area of the containing vessel in a unit time. Consequently, the pressure will decrease.

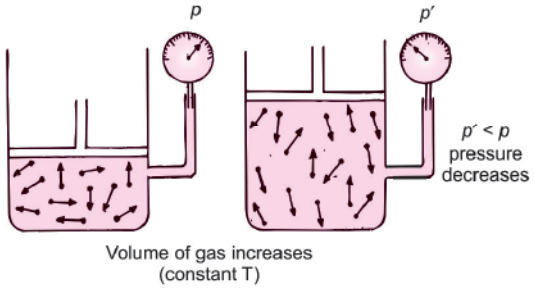

Fig. 22. Illustration of Boyle's law.

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For example, if the volume is made double, the number of molecules striking the unit area of the wall will become about one half. As a result, the pressure of the gas will be reduced to one half of its original value. On the other hand, if volume is decreased, there will be more molecules in a given volume and hence pressure will increase. For example, if volume is made one half, the number of molecules striking per unit area of the wall will be twice under new conditions. Consequently, the pressure will become about double of its original pressure. Thus, it can be concluded that *at given temperature, the pressure exerted by a gas is inversely proportional to the volume.* This is **Boyle's law.**

This can also be easily proved with the help of kinetic gas equation. We have derived from kinetic gas equation,

$$\frac{1}{2}m\overline{u^2} = \frac{3}{2}kT$$

$$pV = \frac{1}{3}Nm\,\overline{u^2}$$

or $$pV = \frac{2}{3}\frac{1}{2}\left(\frac{N}{V}\right)m\overline{u^2}$$

$$= \frac{2}{3}\left(\frac{N}{V}\right)\frac{1}{2}m\overline{u^2}$$

$$= \frac{2}{3}\left(\frac{N}{V}\right)\frac{3}{2}kT$$

or $$pV = N\,kT = \text{Constant}$$

$$\therefore \quad p \propto \frac{1}{V}$$

From this, it is clear that for a fixed number of gas molecules (equivalent to fixed amount , $n = {}^{N}/_{N_A}$) and at constant temperature, pressure is inversely proportional to volume.

This is **Boyle's law.**

2. Charles' law. When temperature of the gas is increased, the kinetic energy of the molecules increases ($\frac{1}{2}mv^2 \propto T$). As a result, the velocity of the molecules increases and consequently, they collide with the walls of the container more frequently and more vigorously. Therefore, the pressure of the gas is expected to increase. However, if pressure is to be kept constant, the number of molecular collisions on the walls of the container must be kept same. This is only possible if the volume of the gas increases, *i.e.* gas expands. On the other hand, if the temperature is decreased, the average velocity of the molecules decreases and, therefore, the pressure decreases. To keep the pressure constant, volume of the gas must decrease so that number of collisions per unit area remains same. Thus, it can be concluded that "*at given pressure, volume of the gas increases with rise in temperature, and decreases with fall in temperature*". Hence, *volume is directly proportional to temperature at constant pressure*. This is **Charles' law.**

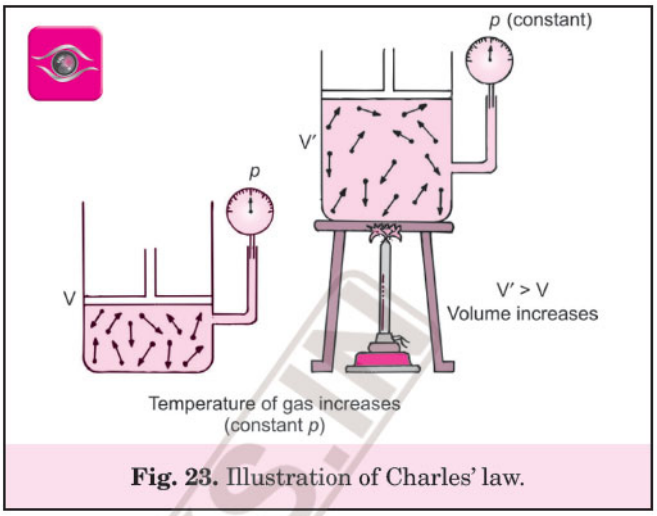

Fig. 23. Illustration of Charles' law.

This can also be proved from kinetic gas equation. We have derived that

$$pV = \frac{2}{3}E_k$$

But $$E_k \propto T$$

$$\therefore \quad pV \propto T$$

At constant pressure,

$$V \propto T$$

This is **Charles' law.**

3. Dalton's law. The pressure of a gas is due to the striking of gas molecules on the walls of the container. Because of the absence of attractive forces, the molecules of each gas behave independently of the molecules of other gases in the mixture. Therefore, no molecule is influenced by others in its collisions with the walls of the container. The molecules of one gas contribute towards the total pressure as if the molecules of other gas were not there. Thus, *the total pressure of a mixture of gases would be the sum of the partial pressures of the gases.* This is **Dalton's law.**

MAXWELL-BOLTZMANN DISTRIBUTION OF MOLECULAR SPEEDS

A gas consists of tiny particles (atoms or molecules) separated from one another by large empty spaces. These particles are constantly moving in all directions. During their motion, they collide with one another and

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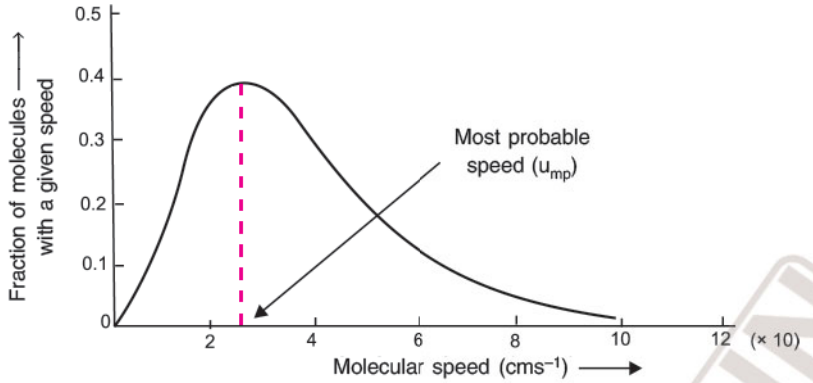

Fig. 24. Maxwell-Boltzmann's distribution of speeds at a particular temperature.

also with the walls of the container. As a result of collisions, the speed and the direction of the molecules go on changing. Thus, all the molecules present in given sample of a gas do not possess the same speed. The speeds of individual molecules are different and are distributed over a wide range. Even if all the particles had same speed initially, due to molecular collisions, they will have different speeds. The speeds of different molecules also go on changing. However, the distribution of speeds among different molecules remains the same at a particular temperature although the individual speeds of the molecules may change.

Thus, the fraction of the molecules with a particular speed remains constant. This is known as distribution of speeds and also as **Maxwell Boltzmann distribution law** because they were the first to formulate it. Maxwell and Boltzmann plotted the fraction of molecules *i.e.*, $\frac{\Delta N}{N}$ (along y-axis) having different speeds against the speeds of the molecules (along x-axis). The curve so obtained is shown in Fig. 24 and is known as **Maxwell's distribution curve.**

The important features of Maxwell's distribution curve can be summed up as follows :

(i) The fraction of molecules with very low or very high speeds is very small.

(ii) The fraction of molecules possessing higher and higher speeds goes on increasing till it reaches the peak and then it starts decreasing.

(iii) The maximum fraction of molecules possesses a speed, corresponding to the peak in the curve. The speed corresponding to the peak in the curve is called ***most probable speed (u_{mp}).***

Thus, the **most probable speed** of a gas is the *speed possessed by the maximum fraction of gas molecules at a given temperature. It is generally denoted by* u_{mp}.

It may be noted that as long as the temperature of a gas is constant, the fraction having the speed equal to most probable speed remains the same but the molecules having this speed may not be the same. In fact, the molecules keep on changing their speed as a result of collisions.

It may be noted that the speed distribution at a particular temperature also depends upon mass of the molecules. At the same temperature, gas molecules with heavier mass have slower speed than lighter gas molecules. For example, lighter nitrogen molecules move faster than the heavier chlorine molecules. Therefore, nitrogen molecules have higher value of most probable speed than chlorine molecules at any given temperature. The molecular speed distribution curves for chlorine and nitrogen are shown in Fig. 25.

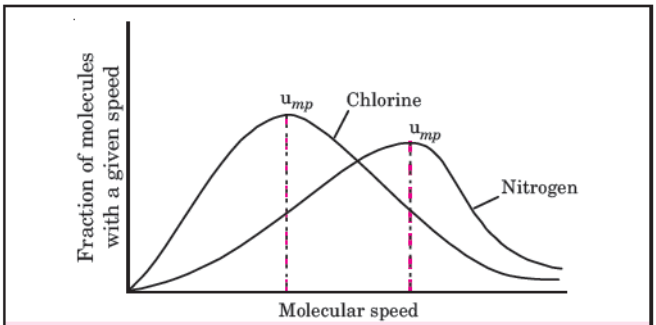

Fig. 25. Distribution of molecular speeds for chlorine and nitrogen at 300 K.

Effect of temperature on the distribution of speeds. As already discussed, the increase in temperature of the gas results into the increase in the molecular motion. Consequently, the value of the most probable speed (u_{mp}) increases with increase in temperature. In fact, the entire distribution curve shifts towards right as the temperature rises. In other words, the curve broadens at higher temperature as shown in Fig. 26. However, it must be remembered that if the temperature remains constant, there is no change in the distribution of speeds among the molecules.

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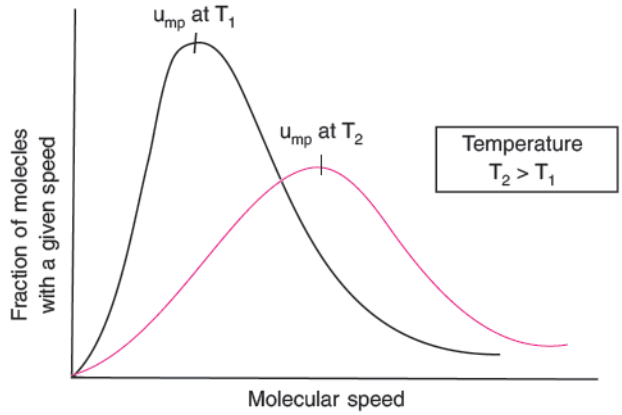

Fig. 26. Distribution of speeds at two different temperatures.

Note. Apart from most probable speed (discussed above) there are two other terms which are commonly used for the gaseous molecules. The three types of speeds are (*i*) *most probable speed* (*ii*) *average speed* and (*iii*) *root mean square speed*.

(*i*) Most probable speed (u_{mp}). *It is the speed possessed by maximum fraction of molecules of a gas at a particular temperature.*

(*ii*) Average speed. *It is the average of the different speeds of all the molecules present in a given sample of gas.* If there are N number of molecules in a sample and their individual speeds are u_1, u_2, u_3 ..... then average speed (u_{av}) is

$$u_{av} = \frac{u_1 + u_2 + u_3 + ...}{N}$$

Alternatively, if u_1 is the speed of N_1 molecules, u_2 is the speed of N_2 molecules, u_3 is the speed of N_3 molecules, and so on, then average speed is

$$u_{av} = \frac{N_1u_1 + N_2u_2 + N_3u_3 + ...}{N_1 + N_2 + N_3 + ...}$$

(*iii*) Root mean square speed. *It is the square root of the mean of the squares of different speeds of the molecules of a gas.* It is represented as $u_{r.m.s}$. If u_1, u_2, u_3.... are the individual speeds of N molecules, then

$$u_{r.m.s.} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + ...}{N}}$$

Alternatively, if u_1 is the speed of N_1 molecules, u_2 is the speed of N_2 molecules, u_3 is the speed of N_3 molecules, then

$$u_{r.m.s.} = \sqrt{\frac{N_1u_1^2 + N_2u_2^2 + N_3u_3^2 + ...}{N_1 + N_2 + N_3 + ...}}$$

The root mean square velocity is the direct measure of the average kinetic energy of gas molecules.

REMEMBER

Root mean square speed, average speed and the most probable speed have following relationship :

$$u_{r.m.s} > u_{av} > u_{mp}$$

These three types of speeds are shown in Fig. 27.

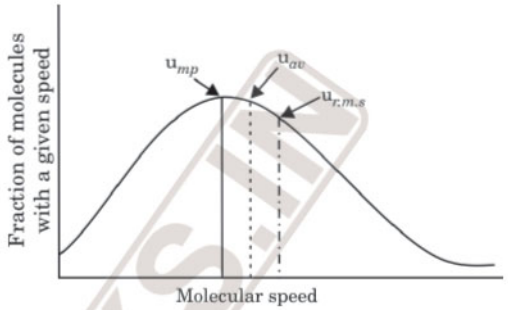

Fig. 27. Different types of speeds in Maxwell – Boltzmann distribution of speeds curve.

Relationship between different types of speeds

The root mean square speed ($\overline{u}_{r.m.s}$), most probable speed (u_{mp}) and average speed (u_{av}) are given by the expressions :

$$\text{Most probable speed, } u_{mp} = \sqrt{\frac{2RT}{M}}$$

$$\text{Average speed, } u_{av} = \sqrt{\frac{8RT}{\pi M}}$$

$$\text{Root mean square speed, } u_{r.m.s.} = \sqrt{\frac{3RT}{M}}$$

The three speeds are related as :

Average speed (u_{av}) = 0.9213 × Root mean square speed ($u_{r.m.s.}$)

Most probable speed (u_{mp}) = 0.816 × Root mean square speed ($u_{r.m.s.}$)

or $u_{mp} : u_{av} : u_{r.m.s.} = 1 : 1.128 : 1.224$

The root mean square speed is commonly used and can be calculated from the following relations :

$$u_{r.m.s.} = \sqrt{\frac{3RT}{M}} \text{ or } \sqrt{\frac{3pV}{M}} \text{ or } \sqrt{\frac{3p}{\rho}}$$

SOLVED EXAMPLES

❑ **Example 40.**

Calculate the kinetic energy of 2 g of oxygen at –23°C.

Solution: Kinetic energy is given as

$$E_k = \frac{3}{2}nRT$$

$$n = \frac{2}{32} = \frac{1}{16} \text{ mol,}$$

$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, $T = 273 - 23 = 250$ K

$$E_k = \frac{3}{2} \times \frac{1}{16} \times 8.314 \times 250 = \mathbf{194.86\ J}$$

❑ **Example 41.**

Calculate the total and average kinetic energy of 32 g of methane molecules at 27°C. (R = 8.314 J K^{-1} mol^{-1}).

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Solution: Average kinetic energy per molecule

$$\overline{E}_{Kinetic} = \frac{3}{2}k_bT$$

$$= \frac{3}{2}\frac{R}{N_A}T$$

$R = 8.314\ J\ K^{-1}\ mol^{-1}$, $N_A = 6.022 \times 10^{23}$, $T = 27 + 273 = 300\ K$

$$\therefore \quad \overline{E}_{Kinetic} = \frac{3}{2} \times \frac{8.314}{6.022 \times 10^{23}} \times 300$$

$$= 6.21 \times 10^{-21}\ J$$

Total kinetic energy,

$$E_k = \frac{3}{2}nRT$$

$$n = \frac{32}{16} = 2\ mol, R = 8.314\ J\ K^{-1}\ mol^{-1}, T = 300\ K$$

$$\therefore \quad E_k = \frac{3}{2} \times 2\ mol \times 8.314\ J\ K^{-1}\ mol^{-1} \times 300\ K$$

$$= \mathbf{7482.6\ J}$$

❑ **Example 42.**

A gas consists of 4 molecules with a velocity of 5 m s^{-1}, 10 molecules with a velocity of 3 m s^{-1} and 6 molecules with a velocity of 6 m s^{-1}. Calculate their average velocity, root mean square velocity and most probable velocity.

Solution:

$$\text{Average velocity} = \frac{4 \times 5 + 10 \times 3 + 6 \times 6}{4 + 10 + 6} = \mathbf{4.3\ m\ s^{-1}}$$

Root mean square velocity

$$= \sqrt{\frac{4 \times (5)^2 + 10 \times (3)^2 + 6 \times (6)^2}{4 + 10 + 6}}$$

$$= \sqrt{\frac{100 + 90 + 216}{20}} = \mathbf{4.50\ m\ s^{-1}}$$

Most probable velocity $= 0.816 \times u_{r.m.s.}$

$= 0.816 \times 4.50 = \mathbf{3.67\ m\ s^{-1}}$

❑ **Example 43.**

Calculate the root mean square speed of methane molecules at 27°C.

Solution: Root mean square speed,

$$u_{r.m.s.} = \sqrt{\frac{3RT}{M}}$$

$T = 27 + 273 = 300\ K$, $M = 16$, $R = 8.314 \times 10^7$

$$u_{r.m.s.} = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{16}}$$

$$= 683.9 \times 10^2\ cm\ s^{-1}$$

$$= \mathbf{683.9\ m\ s^{-1}}$$

❑ **Example 44.**

Nitrogen molecule (N_2) has radius of about 0.2 nm. Assuming that nitrogen molecule is spherical in shape, calcualte

(a) volume of a single molecule of N_2.

(b) the percentage of empty space in one mole of N_2 gas at S.T.P.

Solution: (*a*) The volume of a sphere $= \frac{4}{3}\pi r^3$

where r is the radius of the sphere.

For N_2 molecule, $r = 0.2\ nm = 0.2 \times 10^{-9}\ m = 2 \times 10^{-8}\ cm$

$$\text{Volume of a molecule of } N_2 = \frac{4}{3} \times \frac{22}{7} \times (2 \times 10^{-8})^3\ cm^3$$

$$= \mathbf{3.35 \times 10^{-23}\ cm^3}$$

(*b*) To calculate the empty space, let us first find the total volume of 1 mole (6.02×10^{23} molecules) of N_2.

Volume of 6.02×10^{23} molecules of $N_2 = 3.35 \times 10^{-23} \times 6.02 \times 10^{23} = 20.17\ cm^3$

Now, volume occupied by 1 mole of gas at S.T.P. = 22.4 litre = $22400\ cm^3$

Empty volume = Total volume of gas – Volume occupied by molecules

$= (22400 - 20.17)\ cm^3$

$= 22379.83\ cm^3$

$$\therefore \text{ Percentage empty space} = \frac{\text{Empty space}}{\text{Total volume}} \times 100$$

$$= \frac{22379.83}{22400} \times 100$$

$$= \mathbf{99.9\%}$$

Thus, **99.9% of space of 1 mole of N_2 at S.T.P. is empty.**

❑ **Example 45.**

The average velocity of gas molecules is 400 ms^{-1}. Calculate its r.m.s. velocity at the same temperature. *(I.I.T. 2003)*

Solution: Average speed, $u_{av} = \sqrt{\frac{8RT}{\pi M}}$

Root mean square speed, $u_{r.m.s.} = \sqrt{\frac{3RT}{M}}$

$$\therefore \quad \frac{u_{r.m.s}}{u_{av}} = \sqrt{\frac{3RT}{M}} \Big/ \sqrt{\frac{8RT}{\pi M}}$$

$$\sqrt{\frac{3\pi}{8}} = \sqrt{\frac{3 \times 3.143}{8}} = 1.085$$

$$\therefore \quad u_{r.m.s} = 1.085 \times u_{av}$$

$$= 1.085 \times 400 = \mathbf{4.34\ ms^{-1}}.$$

Practice Problems

44. Calculate the kinetic energy of 2 moles of an ideal gas at 27°C.

45. What is the average kinetic energy of a gas molecule at 27°C ?

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46. Calculate the temperature at which kinetic energy of 0.5 mole of Cl_2 gas is 2.182 kJ.

47. At what temperature will the root mean square velocity of sulphur dioxide be same as that of methane at 27°C ?

48. At what temperature will the root mean square velocity of methane become double of its value at N.T.P.?

49. Calculate the r.m.s. velocity of argon (atomic mass = 40) at N.T.P.

Answers to Practice Problems

44. 7.48 kJ **45.** 6.21×10^{-21} J
46. 76.9°C **47.** 927°C
48. 819°C **49.** 4.127×10^4 cm sec^{-1}

Hints & Solutions on page 58

add on

Conceptual Questions 1

CONCEPTUAL QA

Q. 1. How is the pressure of a gas related to its density at a particular temperature ?

Ans. Pressure is related to density of a gas as :

$$p = \frac{\rho RT}{M}$$

i.e., pressure is directly proportional to density of the gas at a particular temperature.

Q. 2. Water is not used in place of mercury in barometers. Comment.

Ans. In water barometer, very long column (hdg) will be needed because density of water is very low in comparison to mercury.

Q. 3. Why is it not possible to cool a gas to 0 K ?

Ans. This is because all gases condense to liquids or solids before this temperature is reached.

Q. 4. What is the value of molar gas volume (in litres) at NTP for an ideal gas ?

Ans. At NTP, the molar gas volume for an ideal gas is 22.4 L.

Q. 5. Arrange solid, liquid and gas in order of increasing energy ?

Ans. Energy follows the order :

solid < liquid < gas

Q. 6. What is the ratio of average molecular kinetic energy of CO_2 to that of SO_2 at 27°C ?

Ans. Average kinetic energy depends only on temperature and not on the nature of the substance. Thus, the ratio is 1 : 1.

Q. 7. Dry air is heavier than wet air. Why?

Ans. The average molecular mass of dry air is

$$M(\text{dry air}) = \frac{\%\text{ of } N_2 \times 28 + \%\text{ of } O_2 \times 32}{100}$$

Average molecular mass of wet air is

$$M(\text{wet air}) = \frac{\%\text{ of } N_2 \times 28 + \%\text{ of } O_2 \times 32 + \%\text{ of } H_2O \times 18}{100}$$

Therefore, molecular mass of dry air will be more than the molecular mass of wet air.
Since molecular mass of dry air is more than that of wet air, it is heavier.

Q. 8. At what temperature will oxygen molecules have the same K.E. as ozone molecules at 30°C ?

Ans. At 30°C, kinetic energy depends only on absolute temperature and not on the nature of the gas.

Q. 9. How is the mole fraction of a gaseous component related to its partial pressure and the total vapour pressure ?

Ans. Mole fraction of gaseous component = $\frac{\text{Partial pressure}}{\text{Total pressure}}$

Q. 10. What type of graph would you get when PV is plotted against P at constant temperature ?

Ans. A straight line parallel to pressure axis.

Q. 11. Why are vegetables cooked with difficulty at a hill station ?

Ans. The atmospheric pressure is less and so boiling point is lowered.

Q. 12. What would be the S.I. unit for the quantity pV^2T^2/n ?

Ans. $\frac{pV^2T^2}{n} = \frac{(Nm^{-2})\,(m^3)^2(K)^2}{mol} = Nm^4\,K^2\,mol^{-1}$

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Q. 13. A manometer is connected to a gas containing bulb. The level of mercury in open arm is 2.6 cm lower than that in the other arm of the manometer. What is the pressure of the gas if the atmospheric pressure is 752 mm Hg?

Ans. Since level in the open arm of the manometer is lower than that in the arm connected to the gas bulb, this means that atmospheric pressure is greater than the pressure of the gas by difference of the two levels.

$\therefore$ Pressure of gas = 752 – 26 = 726 mm Hg

Q. 14. Name the energy which arises due to motion of atoms or molecules in a body. How is this energy affected when the temperature is increased?

Ans. Thermal energy. It is a measure of average kinetic energy of particles. It increases with increase of temperature.

Q.15. At what temperature will both the Celsius and Fahrenheit scale read the same value?

Ans. Suppose both read the same value as x.

$$C^\circ = \frac{5}{9}(F^\circ - 32) \quad \text{or} \quad x = \frac{5}{9}(x - 32)$$

$$9x = 5x - 160 \quad \text{or} \quad 4x = -160 \quad \therefore x = -40^\circ$$

Q. 16. Calculate the height of a column of water equivalent to 1 atmosphere. (density of Hg = 13.6 g cm^{-3})

Ans. 1 atm = 76 cm of Hg

$p = h_1 d_1 g$ (mercury) $= h_2 d_2 g$ (water) or

$76 \times 13.6 = h_2 \times 1$

$h_2 = 1033.6$ cm or $= 10.336$ m.

Q.17. Is Dalton's law of partial pressures valid for a mixture of SO_2 and O_2?

Ans. No, because SO_2 and O_2 react chemically.

BEHAVIOUR OF REAL GASES : DEVIATIONS FROM IDEAL GAS BEHAVIOUR

A gas which obeys the general gas equation ($pV = nRT$) and other gas laws at all temperatures and pressures is called an **ideal gas** or **perfect gas.** However, none of the actually known gases obey this equation over the entire range of temperatures and pressures. At best, the gases show ideal behaviour at low pressures and high temperatures. As the pressure becomes high and temperature becomes low, more and more deviations are observed from general gas equation and other gas laws.

Deviations of Real Gases

The gas which does not obey general gas equation and other gas laws at all temperatures and pressures is called **non-ideal gas** or **real gas.**

All gases which are actually known to exist such as oxygen, nitrogen, carbon dioxide, etc. are real gases and they show ideal behaviour to different extents. Most of these, show ideal behaviour at low pressures and high temperatures. Amagat Andrews and other scientists made extensive study of the behaviour of various gases under different conditions of temperatures and pressures. They concluded that real gases do not obey the general gas equation under all conditions of temperature and pressure.

To test the behaviour of real gases, we plot pV versus p plot of gases at constant temperature. According to Boyle's law, pV will be constant and pV versus p plots at all pressures will be straight line parallel to x-axis. Fig. 28. shows such a plot of several gases at 273 K.

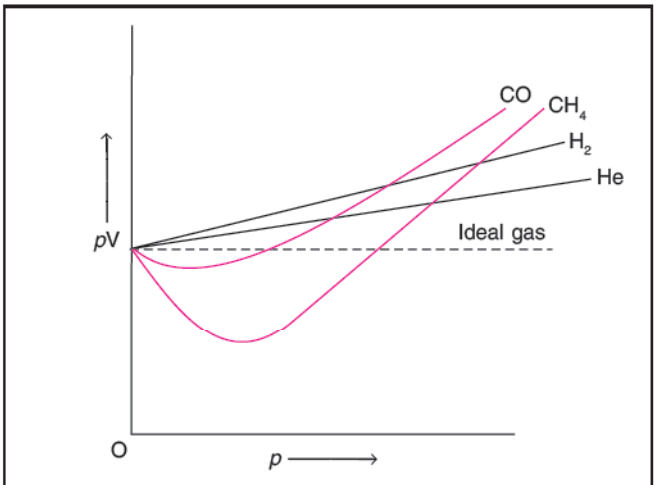

Fig. 28. Plot of pV vs p for real gases and ideal gas.

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It can be seen easily from Fig. 28 that at constant temperature pV versus p plot for real gases is not a straight line. There are significant deviations from ideal behaviour. Two types of curves are observed :

(i) For gases such as dihydrogen (H_2) and helium (He) as the pressure increases the value of pV also increases.

(ii) For gases such as carbon monoxide (CO) and methane (CH_4), first there is a negative deviation from ideal behaviour so that pV decreases with increase in pressure. It reaches to a minimum value characteristic of a gas. After that pV value starts increasing. The curve crosses the line for ideal gas and after that shows positive deviation continuously.

Thus, real gases do not follow ideal gas equation perfectly at all conditions. Deviations from ideal behaviour also become clear when pressure versus volume plots are drawn. The pressure vs volume plot of experimental data (real gases) and that theoretically calculated from Boyle's law (for ideal gas) should coincide if all gases behave ideally. This is shown in Fig. 29.It is clear that they do not coincide. At high pressures, the measured volume is more than the calculated volume. However, at low pressures measured and calculated volumes almost approach each other.

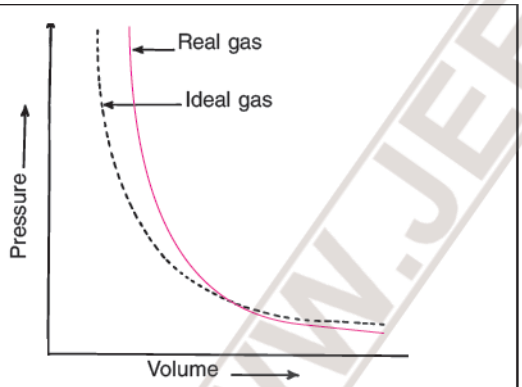

Fig. 29. Plot of p against V for ideal and real gases.

Measuring deviations from Ideal Behaviour

Effect of pressure

A simple way to study deviations of real gases from ideal behaviour is to plot a graph between $\frac{pV}{nRT}$ and p.

The quantity $\frac{pV}{nRT}$ is called **compressibility factor** and is denoted by Z.

$$\text{Compressibility factor, } Z = \frac{pV}{nRT}$$

For ideal gases, Z = 1 under all conditions of temperature and pressure. This means that

$$\frac{pV}{nRT} = 1 \text{ for ideal gases or } pV = nRT$$

In other words, pV *is always equal to* nRT *and this corresponds to ideal gas behaviour.* For real gases, Z may be less than 1 or more than 1. Thus,

$pV \neq nRT$ for real gases.

The $\frac{pV}{nRT}$ versus p plots for some common gases such as H_2, N_2, O_2, He, CH_4 and CO_2 are shown in Fig. 30.

It is clear from the figure that Z has values greater than and less than one (ideal behaviour).

(i) If **Z < 1**, it is called **negative deviation.** It means that *the gas is more compressible than expected from ideal behaviour.*

(ii) If **Z > 1**, it is called **positive deviation.** It means that *the gas is less compressible than expected from ideal behaviour.*

It is observed that the deviations are low at low pressure. This means that the equation $pV = nRT$ (ideal gas equation) is almost valid at low pressures for all gases.

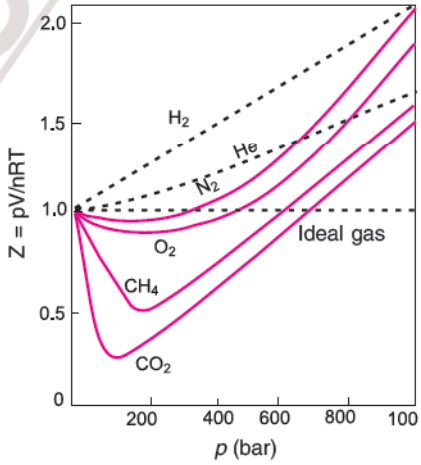

Fig. 30. Plot of the compressibility factor, Z vs p.

$Z = \frac{pV}{nRT}$ as a function of p for some gases.

At high pressures, Z is always greater than unity. The extent of deviation at any pressure or temperature depends upon the nature of the gas. Moreover, Z approaches unity as pressure approaches zero.

(a) For H_2 and He, Z is always greater than 1 (shown dotted). This means that *these gases are less compressible than expected from ideal behaviour at all pressures.*

(b) For N_2, O_2, CH_4 and CO_2, Z is less than 1 at low pressures and greater than 1 at higher pressures. This means that *these gases are more compressible at low pressures and less compressible at high pressures than expected from ideal behaviour.*

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Effect of temperature

The effect of temperature on the behaviour of real gases can be seen by comparing the behaviour of N_2 gas at different temperatures. The value of pV_m (where V_m is molar volume of gas, $V_m = V/n$) at different temperatures is shown in Fig. 31. In this plot, the dotted lines represent ideal behaviour at that temperature. It is clear from the figure that dip in the curves goes on becoming smaller and smaller as the temperature increases. This means that **the deviations from ideal behaviour become less and less with increase in temperature.** At a certain temperature, the minimum in the curve vanishes and the curve remains horizontal for an appreciable range of pressure (ideal behaviour).

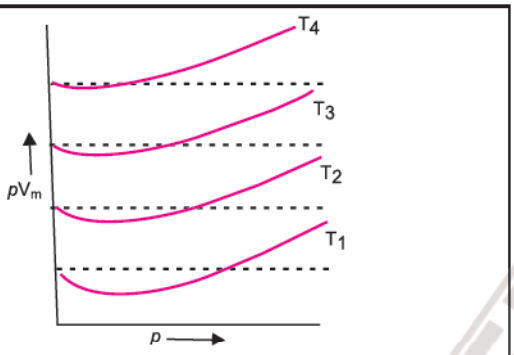

Fig. 31. Plot of pV against p for N_2 at different temperatures $T_4 > T_3 > T_2 > T_1$.

So we have learnt that the behaviour of the gas becomes more ideal when pressure in very low. Upto what pressure, a gas will follow ideal gas law depends upon the nature of the gas and its temperature. The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called **Boyle temperature or Boyle point.**

The Boyle temperature is different for different gases. For example, the Boyle temperature for N_2 is 59°C and for hydrogen is –165°C.

Above the Boyle point, real gases show positive deviations from ideality and Z values are greater than one. The forces of attraction between the molecules are very small. Below Boyle temperature, real gases first show decrease in Z value with increasing pressure, which reaches a minimum value. On further increase in pressure, the value of Z increases continuously. This shows that at low pressures and high temperatures gases show ideal behaviour. These conditions are different for different gases.

We can have more insight of the significance of Z as :

$$Z = \frac{pV}{nRT}$$

If the gas shows ideal behaviour, then

$$V_{ideal} = \frac{n\,R\,T}{p}$$

Substituting the value of $\frac{n\,R\,T}{p}$ in the above equation, we get,

$$Z = \frac{V_{real}}{V_{ideal}}$$

Thus, ***compressibility factor*** *is the ratio of actual molar volume of a gas to the molar volume of it, if it were an ideal gas at that temperature and pressure.*

Thus, we conclude

- **At best the real gases show ideal behaviour at low pressures and fairly high temperatures.**
- **At low temperatures and high pressures, the gases differ significantly from ideal behaviour.**

Causes of Deviations from Ideal Behaviour

We have studied that real gases show marked departure from ideal behaviour at low temperature and high pressure.

(*i*) Why do gases deviate from ideality ?

(*ii*) Why does the ideal gas law fail at high pressures and low temperatures ?

These are the important questions which come to our mind. In order to explain the deviations from ideality, van der Waal pointed out that the following two assumptions in kinetic theory are faulty :

Faulty Assumptions in Kinetic Theory of Gases

(*i*) *The volume occupied by the gas molecules is negligibly small in comparison to the total volume of the gas.*

(*ii*) *The forces of attraction between the gas molecules are negligible.*

The above two assumptions are valid only if the *pressure is low* or the *temperature is high* so that the distance between the molecules is large. However, as the pressure is high or the temperature is low, the gas molecules come close together and the distance between them decreases. Under these conditions:

(*i*) The volume occupied by the gas is small so that the volume occupied by the molecules may not be neglected.

(*ii*) The distance between the molecules is small so that the attractive forces between them may not be negligible.

Corrections of Deviations — van der Waals equation for Real Gases

To account for the behaviour of real gases, it becomes necessary to apply suitable corrections to the ideal gas equation, $pV_m = RT$, so as to make it applicable to real gases. The ideal gas equation was modified by van der Waals. The modified equation of state which explains the deviations of real gases from ideality is known as **van der Waals equation of state.**

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Van der Waals applied the following corrections to the ideal gas equation :

***(i)* Correction due to volume.** The volume occupied by the molecules cannot be neglected in comparison to the total volume. This means that the molecules are not free to move in whole of volume V but the free volume is less than the observed volume. In other words, the ideal volume of a gas is less than observed volume.

It was, therefore, suggested by van der Waals' that a suitable correction term may be subtracted from the observed volume. The correction term for one mole of the gas is 'b' where 'b' is a constant depending upon the nature of the gas and is known as **excluded volume** or **co-volume.** Thus, if V be the volume occupied by 1 mole of the gas, then the volume available to the molecules for the movement, *i.e.* corrected volume is

$$V_{corrected} = (V - b) \text{ for one mole}$$

For n moles of the gas, the correction term is nb so that corrected volume is given by :

$$V_{corrected} = (V - nb) \text{ for } n \text{ moles}$$

It may be noted that b is not equal to actual volume of the molecules but it has been calculated to be **four times the actual volume of the molecules.**

If the molecules are assumed to be spheres having radius r, then volume of one molecule of the gas is $\frac{4}{3}\pi r^3$. The excluded volume or co-volume, b is

$$b = 4 \times \text{Volume of one molecule}$$

or $$b = 4 \times \frac{4}{3}\pi r^3 \text{ (for one molecule)}$$

or $$b = 4 \times \frac{4}{3}\pi r^3 \times \text{Avogadro number (for one mole)}$$

▶ EXCLUDED VOLUME IS FOUR TIMES THE ACTUAL VOLUME OF A MOLECULE

Let us assume that the molecules are spherical with radius equal to r. Then volume of the molecules is $\frac{4}{3}\pi r^3$. As is clear from the figure, the distance of closest approach of two molecules is $2r$. Therefore, two molecules cannot approach each other more closely than the distance $2r$. Thus, if we consider only bimolecular collisions, then the volume occupied by a sphere of radius $2r$ represents the excluded volume per pair of molecules. Thus,

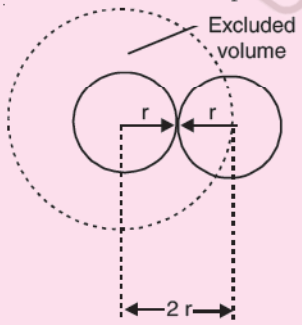
$$\text{Excluded volume per pair of molecules} = \frac{4}{3}\pi(2r)^3$$

$$\text{Excluded volume per molecule} = \frac{1}{2}\left[\frac{4}{3}\pi(2r)^3\right]$$

$$= \frac{1}{2}\left[8 \times \frac{4}{3}\pi r^3\right]$$

$$= 4 \times \frac{4}{3}\pi r^3$$

$$= 4 \times \text{Volume occupied by a molecule.}$$



***(ii)* Correction due to intermolecular forces.** As discussed earlier, some attractive forces exist between the molecules of the real gases. Consider a molecule of a gas in the middle of the container (Fig. 32). The molecule is being attracted uniformly by the neighbouring molecules. The attractive forces neutralise one another and there is no resultant pull on the molecule. On the other hand, when a molecule approaches the wall of the container, it experiences an inward pull as a result of the attractive forces exerted by the neighbouring molecules inside the vessel. Thus, the molecule strikes the wall with a lesser force than it would have done if there were no attractive forces.

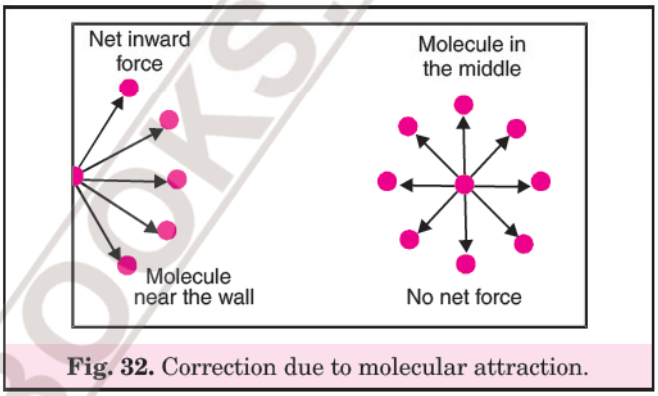


Fig. 32. Correction due to molecular attraction.

Therefore, the observed pressure is less than the ideal pressure. Consequently, some correction term should be added to the observed pressure in order to calculate ideal pressure.

Hence, corrected pressure, $p_{corrected}$ is given by :

$$p_{corrected} = p + p'$$

where p is the observed pressure and p' is the correction term.

Van der Waals suggested that to correct the pressure, the pressure term p is equal to $\frac{a}{V^2}$ for one mole and $\frac{an^2}{V^2}$ for n moles where 'a' is a constant which depends upon the nature of the gas.

Thus,

$$p_{corrected} = p + \frac{a}{V^2} \text{ for one mole}$$

$$p_{corrected} = p + \frac{an^2}{V^2} \text{ for } n \text{ moles}$$

Substituting the corrected values of volume and pressure in ideal gas equation, $PV = nRT$, we get

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \text{ for } n \text{ moles}$$

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \text{ for one mole}$$

These equations are called **van der Waals equations** of state.

Significance and units of *a* and *b*

The constants a and b are called van der Waals'

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constants and their values depend upon the nature of the gas.

(*i*) Van der Waals constant '*a*'.

The constant 'a' measures the forces of attraction between the molecules of a gas. Greater the value of '*a*' greater is the strength of van der Waals interactions. As expected the value of '*a*' for the gas with lower molecular weight, such as H_2 and He is quite low whereas, the value of '*a*' for gases with high molecular weights is relatively high. It may be noted that the greater value of '*a*' of a gas also reflects its greater tendency to be liquefied. Therefore, *the gases having higher values of 'a' will be easily liquefied.*

(*ii*) Van der Waals constant '*b*'.

The constant '*b*' relates to incompressible volume of the molecules and measures the effective size of gas molecules. It may be noted that '*b*' is not equal to actual volume of the molecule but it is four times the actual volume of molecules.

Units of van der Waals Constants.

Now, we have seen that

$$p' = \frac{an^2}{V^2}$$

or $$a = \frac{p'V^2}{n^2} = \frac{(\text{pressure}) \times (\text{volume})^2}{(\text{moles})^2}$$

Therefore, the units of '*a*' are **atm L^2 mol^{-2} or bar dm^6 mol^{-2}**

Similarly, $v = nb$ or $b = \frac{v}{n}$

Therefore, the units of '*b*' are **L mol^{-1} or dm^3 mol^{-1}.**

▶ APPLICABILITY OF VAN DER WAALS EQUATION

The van der Waals' equation is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

(*i*) **At low pressures.** At low pressures, the volume is sufficiently large and therefore, *b* can be neglected in comparison to V so that

$$\left(p + \frac{a}{V^2}\right) V = RT$$

or $$pV = RT - \frac{a}{V}$$

or $$\frac{pV}{RT} = 1 - \frac{a}{RTV}$$

Thus, at low pressures, $\frac{pV}{RT}$ *i.e.* Z is less than one. As pressure increases (V decreases), the term $\frac{a}{RTV}$ increases. Consequently, Z decreases with increase in *p*. *This explains the initial dip in the plot of Z versus p.*

(*ii*) **At high pressure.** When *p* is high, V will be small so that *b* cannot be neglected in comparison to V. But $\frac{a}{V^2}$ may be considered negligible in comparison to *p* so that

$$p(V - b) = RT$$

or $$pV = RT + pb$$

or $$\frac{pV}{RT} = 1 + \frac{pb}{RT}$$

Thus, $\frac{pV}{RT}$ *i.e.* Z is greater than 1 and increases as pressure increases. *This explains that after minima in the curves, the compressibility factor, Z increases continuously with pressure.*

(*iii*) **At high temperature and low pressure.** If temperature is high, V is very large and therefore, *b* as well as $\frac{a}{V^2}$ may be neglected so that equation reduces to ideal gas equation,

$$pV = RT.$$

Exceptional behaviour of H_2 and He. We have seen (Fig. 30) that the behaviour of H_2 and He is exceptional because the compressibility factor always increases with increase in temperature. This is due to the fact that '*a*' for hydrogen and helium is very small indicating that *forces of attraction in these gases are very weak.* Therefore, a/V^2 is negligible at all pressures.

The van der Waals equation, therefore, becomes

$$p(V - b) = RT$$

$$pV - pb = RT$$

or $$pV = RT + pb$$

or $$\frac{pV}{RT} = 1 + \frac{pb}{RT}$$

Thus, $\frac{pV}{RT}$ i.e., Z is always greater than 1 at all values of *p* at constant temperature.

Differences between Ideal gas and Real gas. The main differences between ideal gas and real gas are summed up below :

Ideal gas	Real gas
1. Ideal gas obeys all gas laws under all conditions of temperature and pressure.	1. Real gas obeys gas laws only under low pressure and high temperature.
2. In ideal gas, the volume occupied by the molecules is negligible as compared to the total volume occupied by the gas.	2. In real gas, the volume occupied by the molecules is not negligible as compared to the total volume occupied by the gas.
3. The forces of attraction among the molecules of the gas are negligible.	3. The forces of attraction among the molecules are not negligible at all temperatures and pressures.
4. It obeys ideal gas equation : $pV = nRT$	4. It obeys Van der Waals' equation : $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$

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SOLVED EXAMPLES

Example 46.

One mole of CO_2 occupies 1.5 L at 25°C. Calculate the pressure exerted by the gas using

(i) ideal gas equation

(ii) van der Waals gas equation with $a = 3.6\ L^2$ bar mol^{-2} and $b = 0.04\ L\ mol^{-1}$.

Solution: (*i*) According to ideal gas equation,

$$pV = nRT \quad \text{or} \quad p = \frac{nRT}{V}$$

$n = 1$ mol, $T = 273 + 25 = 298$ K, $V = 1.5$ L, $R = 0.083$ L bar K^{-1} mol^{-1}

$$\therefore\ p = \frac{1\ \text{mol} \times 0.083\ \text{L bar mol}^{-1}\text{K}^{-1} \times 298\ \text{K}}{1.5\ \text{L}}$$

$$= \mathbf{16.49\ bar}$$

(*ii*) According to van der Waals gas equation,

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\text{or} \quad p = \frac{nRT}{(V - nb)} - \left(\frac{an^2}{V^2}\right)$$

$$p = \frac{1\ \text{mol} \times 0.083\ \text{L bar mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}}{(1.5 - 1 \times 0.04)\ \text{L}} - \frac{3.6\ \text{L}^2\ \text{bar mol}^{-2} \times (1\ \text{mol}^2)}{(1.5\ \text{L})^2}$$

$= 16.94 - 1.60 =$ **15.34 bar.**

Example 47.

Calculate the temperature of 2 mol of SO_2 gas contained in a 5L flask at 10 bar pressure. For SO_2, the van der Waals constants are : $a = 6.7$ bar $L^2\ mol^{-2}$ and $b = 0.05642\ L\ mol^{-1}$.

Solution: According to van der Waals equation,

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\text{or} \quad T = \frac{\left(p + \frac{an^2}{V^2}\right)(V - nb)}{nR}$$

$n = 2$ mol, $V = 5$ L, $p = 10$ bar

$a = 6.7$ bar $L^2\ mol^{-2}$, $b = 0.0564$ L mol^{-1}

$$T = \frac{\left(10 + \frac{6.7 \times 2 \times 2}{(5)^2}\right)(5 - 2 \times 0.0564)}{2 \times 0.083}$$

$$= \frac{(10 + 1.072)(5 - 0.1128)}{0.166} = \mathbf{326.6\ K}$$

Example 48.

For oxygen gas, the van der Waals constant b is 0.0318 L mol^{-1}. Calculate the diameter of oxygen molecule.

Solution: Van der Waals constant,

$b = 4 \times$ Volume occupied by molecules in 1 mole of gas

$$= 4 \times \frac{4}{3}\pi r^3 \times 6.023 \times 10^{23}$$

$b = 0.0318\ \text{L mol}^{-1} = 0.0318 \times 10^3\ \text{cm}^3\ \text{mol}^{-1}$

$$0.0318 \times 10^3 = 4 \times \frac{4}{3} \times 3.14 \times r^3 \times 6.023 \times 10^{23}$$

$$\text{or} \quad r^3 = \frac{0.0318 \times 10^3 \times 3}{16 \times 3.14 \times 6.023 \times 10^{23}}$$

$$r = \left(\frac{0.0318 \times 10^3 \times 3}{16 \times 3.14 \times 6.023 \times 10^{23}}\right)^{\frac{1}{3}}$$

$$= 1.47 \times 10^{-8}\ \text{cm}$$

Diameter of oxygen molecule $= 2 \times 1.47 \times 10^{-8}$

$= \mathbf{2.94 \times 10^{-8}\ cm.}$

Example 49.

A vessel of 25 L capacity contains 10 mol of steam under 50 bar pressure. Calculate the temperature of steam using van der Waals equation if for water :

$a = 5.46$ bar $L^2\ mol^{-2}$ and $b = 0.031$ L mol^{-1}.

Solution: Van der Waals' equation is

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\text{or} \quad T = \frac{\left(p + \frac{an^2}{V^2}\right)(V - nb)}{nR}$$

$n = 10$ mol, $V = 25$ L, $p = 50$ bar

$a = 5.46$ bar $L^2\ mol^{-2}$, $b = 0.031$ L mol^{-1}

$$\therefore \quad T = \frac{\left(50 + \frac{5.46 \times 100}{(25)^2}\right)(25 - 0.031)}{10 \times 0.082}$$

$$= \mathbf{1531.7\ K.}$$

Example 50.

Two moles of a real gas confined in a 5L flask exerts a pressure 9.1 atm at a temperature of 27°C. Calculate the value of 'a' given the value of b is 0.052 L mol^{-1}.

Solution:

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$a = \left[\left(\frac{nRT}{V - nb}\right) - p\right] \times \frac{V^2}{n^2}$$

$n = 2$ mol, $V = 5$ L, $p = 9.1$ atm, $R = 0.082$ L atm mol^{-1} K^{-1}, $T = 273 + 27 = 300$ K

$$a = \left[\frac{2 \times 0.082 \times 300}{(5 - 2 \times 0.052)} - 9.1\right] \times \frac{(5)^2}{(2)^2}$$

$$= \left(\frac{49.2}{4.896} - 9.1\right) \times \frac{25}{4}$$

$$= (10.05 - 9.1) \times \frac{25}{4} = 5.94\ \text{atm L}^2\ \text{mol}^{-2}.$$

Example 51.

1 mole of sulphur dioxide occupies a volume of 350 ml at 27°C and 5×10^6 Pa pressure. Calculate

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the compressibility factor of the gas. Is it less or more compressible than an ideal gas ?

Solution: Compressibility factor,

$$Z = \frac{pV}{nRT}$$

n = 1 mol, p = 5 × 10^6 Pa, V = 350 mL = 0.350 × 10^{-3} m^3

R = 8.314 Nm K^{-1} mol^{-1}, T = 27 + 273 = 300 K

$$\therefore\ Z = \frac{5 \times 10^6 \times 0.350 \times 10^{-3}}{1.0 \times 8.314 \times 300} = \mathbf{0.702}$$

SO_2 is more compressible than an ideal gas (which has Z = 1).

Practice Problems

50. Two moles of ammonia were found to occupy a volume of 5L at 27°C. Calculate the pressure using van der Waals equation (a = 4.17 bar L^2 mol^{-2}, b = 0.0371 L mol^{-1}).

51. Compare the temperature of 3 mol of SO_2 at 15 bar occupying a volume of 10L obtained by the ideal gas equation and van der Waals equation (a = 6.7 bar L^2 mol^{-2}, b = 0.0564 L mol^{-1}).

Answers to Practice Problems

50. 9.32 bar

51. 609.8 K,
623.54 K

Hints & Solutions on page 58

LIQUEFACTION OF GASES AND THE CRITICAL PHENOMENA

Gases can be liquefied by lowering the temperature and increasing the pressure. In the middle of the 19th century, a number of gases such as CO_2, SO_2, NH_3, H_2S, N_2O, etc. were liquefied by the combined effect of cooling (lowering the temperature) and compression (increasing the pressure). According to kinetic molecular model of gases, the forces of attraction between the molecules are negligible. When the temperature of the gas is lowered, the kinetic energy of the molecules decreases. As a result, the slow moving molecules come nearer to one another. At a sufficiently low temperature, some of the slow moving molecules cannot resist the force of attraction and they come closer and closer and ultimately the gas changes into the liquid state.

The increase in pressure can also bring the gaseous molecules closer to one another (due to decrease in volume). Therefore, gases can also be liquefied by increasing the pressure. Thus, **gases can be liquefied by decrease of temperature or increase of pressure or by the combined effect of both.** However, the effect of temperature is rather more important than the pressure. The essential conditions for liquefaction of gases were studied by Thomas Andrews in 1869.

Thomas Andrews studied the pressure-volume-temperature relations in gaseous and liquid states of carbon dioxide. He measured the variation of volume of CO_2 with pressure at various constant temperatures and plotted isotherms (p–V relations) of CO_2 gas at different temperatures. Fig. 33 show the plots of pressure *vs*. volume for CO_2 at various constant temperatures obtained by plotting Andrews data. Andrews observed that at high temperatures isotherms look like that of an ideal gas and the gas cannot be liquefied even at very high pressure. As the temperature is lowered, the shape of the curve changes and data shows more and more deviations from ideal behaviour. This is because CO_2 does not behave ideally as the temperature becomes lower and lower.

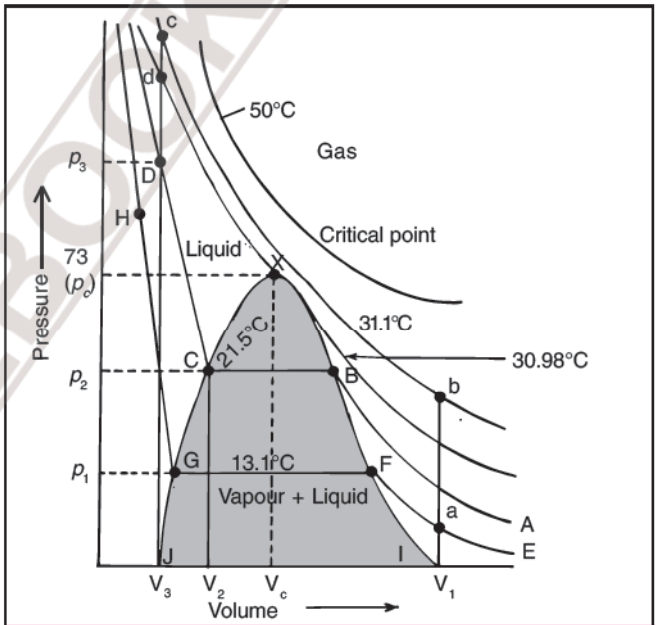

Fig. 33. Isotherms of CO_2 at different temperatures.

It is clear from Fig. 33 that at 50°C, the isotherm for CO_2 is very similar to that for ideal gas. It was observed that at 30.98°C, carbon dioxide remains gas upto 73 atmospheric pressure (as shown point X). At 73 atmospheric pressure, liquid carbon dioxide appears for the first time. This is the highest temperature at which liquid carbon dioxide is observed. Above this temperature, it is gas. It is called **critical temperature.** Further increase in pressure simply compresses the liquid carbon dioxide and the curve represents the **compressibility of the liquid.** It is observed that even a slight compression results in steep rise in pressure indicating very low compressibility of the liquid.

Below 30.98°C, the behaviour of the gas on compression is quite different. For example, at 21.5°C the isotherm ABCD consists of three parts. At point A, carbon dioxide is gas. The volume of the gas decreases along AB as the pressure increases upto B.

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At point B, liquid of a particular volume appears. Further compression does not change the pressure. Liquid and gaseous carbon dioxide co-exist and further application of pressure results in the condensation of more gas until the point C is reached. So, the horizontal portion BC indicates that there is considerable change in volume with a change in pressure indicating process of liquefaction. In other words, the gas condenses to a compact liquid. The condensation would be completed at C. At C when the condensation is completed the isotherm rises steeply as there is very little change in volume of the liquid as pressure increases. In other words, the reduction in volume from C to D corresponds to very high pressure required to compress a liquid into a smaller volume.

As shown in Fig. 33, a slight compression from volume V_2 to V_3 results in steep rise in pressure from p_2 to p_3.

Below 30.98°C (critical temperature) each curve shows the similar trend except that the length of the horizontal line increases at lower temperature. As is clear from the figure, the central horizonal line (FG) at 13.1°C is larger than at 21.5°C (BC). Alternatively, we observe that the horizontal portion becomes smaller as temperature increases. At critical point, the horizontal portion of the curve merges into one point. Thus, we can say that a point like A in Fig. 33 represents gaseous state. A point like D represents liquid state and a point under the dome shaped area (shaded portion, JGCXBFI) represents co-existence of liquid and gaseous carbon dioxide in equilibrium. Andrews also concluded that all the gases under compression at constant temperature (isothermal compression) show the behaviour similar to behaviour of carbon dioxide. Thus, we observe that at 30.98°C the isotherm has a very small flat portion virtually reduced to a point X. Above 30.98°C, there is no flat portion indicating that under all pressures, it remains in gaseous state. Generally, the gases below their critical temperatures are called **vapours.**

Difference between vapour and gas

In terms of critical temperature, a gas can be liquefied below the critical temperature by applying pressure. Therefore, *above the critical temperature, it is a gas but below the critical temperature, it is vapour*.

Thus, Andrews concluded that there is a certain temperature above which a gas cannot be liquefied no matter how high a pressure may be applied. The gas can be liquefied only below this temperature. This characteristic temperature is called **critical temperature.** It is written as T_c. Thus,

critical temperature is the temperature above which a gas cannot be liquefied however high the pressure may be.

For example, the critical temperature of carbon dioxide is found to be 31.1°C. *This means that carbon dioxide cannot be liquefied above this temperature even at pressure of several hundred atmospheres.*

Similarly, critical pressure (p_c) and critical volume (V_c) may be defined as :

- ***Critical pressure is the minimum pressure required to liquefy the gas at the critical temperature.***
- ***Critical volume is the volume occupied by one mole of the gas at critical temperature and pressure.***

The critical constants of some common substances are given in Table 6.

Table 6. Critical constants for some common gases.

Substance	T_c (K)	p_c (bar)	V_c $dm^3\ mol^{-1}$
H_2	33.2	12.97	0.0650
He	5.3	2.29	0.0577
N_2	126.0	33.9	0.0900
O_2	154.3	50.4	0.0744
CO_2	304.15	73.9	0.0956
H_2O	647.1	220.6	0.0450
NH_3	405.5	113.0	0.0723

Importance of Critical Temperature

It is clear from the table that gases like NH_3, CO_2, Cl_2, Br_2, etc. can be easily liquefied by applying pressure because their critical temperatures are above room temperature. However, gases like helium, hydrogen, nitrogen and oxygen cannot be liquefied at ordinary temperature by increasing pressure alone, however high it may be. Such gases were earlier called **permanent gases.** The work of Andrews showed the necessity of cooling such gases below their critical temperature to liquefy them.

Continuity of state

It is possible to convert a gas into a liquid or a liquid into a gas by a process in which only a single state is always present. On joining the ends of the horizontal portions of various isotherms, a boundary curve JGCXBFI, represented by shaded portion is obtained. It has critical point X at its top. Within the area of the boundary curve, both liquid and gaseous states can coexist but outside this area, only one phase, either liquid or gas alone can exist. Suppose, a certain volume of carbon dioxide represented by a point 'a' on 13.1°C isotherm, is heated at constant volume to a temperature at which the pressure increases to a point *'b'*, lying on isotherm at 31.1°C. We can move from point *'b'* to *'c* by compressing the gas at constant temperature along this isotherm (isotherm at 31.1°C). Let the gas be now cooled at constant volume. Its pressure will start decreasing. As soon as we cross the point *'d'* on the critical isotherm we get liquid. So we end up with liquid. But during the transition from gas to liquid, there has never been more than one phase present at any time. The process of change from gaseous state to liquid state (or vice versa), therefore,

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is regarded as **continuous.** Thus, there is continuity between the gaseous and liquid state. To recognise this continuity, the term **fluid** is used for either a liquid or a gas. A liquid can be viewed as a very dense gas. The liquid and gas can be distinguished only when the fluid is below its critical temperature and its pressure and volume lie in the area JGCXBFI (shaded portion). In this situation, the liquid and the gas are in equilibrium and the boundary separating the two phases is visible. In the absence of such a boundary or surface, there is no fundamental way of distinguishing between two states.

At critical temperature, liquid changes into gaseous state imperceptibly and continuously and the surface separating these two phases disappears. A gas below its critical temperature can be liquefied by applying pressure and is called vapour of the substance. Carbon dioxide below its critical temperature is called carbon dioxide vapour.

At the critical points, the densities of a substance in gaseous and liquid states become same. There is no distinction between the gaseous state and the liquid state. No second phase is formed irrespective of the pressure of the system. It may be noted that the dense fluid obtained by compressing a gas when its temperature is higher than its critical temperature is not a true liquid, but it behaves like a liquid in many respects, *i.e.* it has similar density and can act as a solvent. However, it is not strictly a liquid because it never possesses a surface which separates it from a vapour phase. Moreover, it is not like a gas because it is very dense. These fluids above the critical temperature are called **super critical fluids.** These can be used as solvents because these dissolve many organic substances. For example, carbon dioxide above 31.1°C and above 60 bar pressure has a density of about 1 g cm^{-3} and has been used to extract caffeine from coffee beans instead of using chlorofluorocarbons which are not environmental friendly.

Critical constants and van der Waals' Equation

The critical constants may be expressed in terms of van der Waals' constants a and b as :

$$T_c = \frac{8a}{27Rb} \quad ...(i)$$

$$p_c = \frac{a}{27b^2} \quad ...(ii)$$

$$V_c = 3b \quad ...(iii)$$

where R is a gas constant.

Alternately, if p_c, V_c and T_c of a gas are known, it is possible to calculate the values of a, b and R as :

$$b = \frac{V_c}{3} \quad ...(iv)$$

$$a = 3p_cV_c^2 \quad ...(v)$$

and $$R = \frac{8p_cV_c}{3T_c} \quad ...(vi)$$

It may be noted that it is generally difficult to determine V_c accurately and therefore, it is better to calculate a and b from p_c and T_c only

From eq. (*vi*), $V_c = \frac{3RT_c}{8p_c}$

$$\therefore \quad b = \frac{1}{3}\left(\frac{3RT_c}{8p_c}\right) = \frac{RT_c}{8p_c}$$

and $$a = 3p_cV_c^2 = 3p_c\left(\frac{3RT_c}{8p_c}\right)^2 = \frac{27(RT_c)^2}{64p_c}$$

Boyle temperature in terms of van der Waals' constants

$$T_B = \frac{a}{bR}$$

SOLVED EXAMPLES

Example 52.

The critical temperature and pressure for NO gas are 177 K and 64.5 atm respectively. Calculate van der Waals constants 'a' and 'b' for this gas.

Solution: $T_c = 177$ K, $p_c = 64.5$ atm

$$a = \frac{27(RT_c)^2}{64p_c}$$

$$= \frac{27\times(0.082\times177)^2}{64\times64.5}$$

$$= 1.34 \text{ litre}^2 \text{ atm mol}^{-2}$$

$$b = \frac{RT_c}{8p_c} = \frac{0.082\times171}{8\times64.5}$$

$$= 0.02813 \text{ litre mol}^{-1}$$

Example 53.

Calculate the critical temperature of a Van der Waals gas for which p_c is 100 atm and b is 0.050 dm^3 mol^{-1}.

Solution: $T_c = \frac{8a}{27Rb}$

But $a = 3p_cV_c^2 = 3p_c \times (3b)^2 = 27\,p_c\,b^2$

$$\therefore \quad T_c = \frac{8(27p_cb^2)}{27Rb} = \frac{8p_cb}{R}$$

$p_c = 100$ atm, $b = 0.050$ dm^3 mol^{-1}

$$\therefore \quad T_c = \frac{8\times(100 \text{ atm})\times(0.050 \text{ dm}^3\text{mol}^{-1})}{0.082 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}}$$

$$= \mathbf{487.2\ K.}$$

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❑ **Example 54.**

Critical temperature of ammonia and carbon dioxide are 405.5 K and 304.10 K respectively. Which of these gases will liquefy first when you start cooling from 500 K to their critical temperature ?

Solution: Ammonia will liquefy first because its critical temperature will be reached first. Liquefaction of CO_2 will require more cooling.

LIQUID STATE OF MATTER

Liquids have *definite volumes but not definite shapes*. These take the shapes of the container. In terms of kinetic molecular model, *the molecules of liquids are close together and attractive forces between molecules are strong in comparison to those in gases.* However, the intermolecular forces are not strong enough as in solids to have definite shapes. But, they cannot be separated from one another completely and this results in definite volume for liquids. Another important distinction between gases and liquids is the extent of order. In the case of gases, there is a complete random distribution of gas molecules. This corresponds to *disordered state*. In the case of liquids, there is significantly more order or less disorder. But, this order is definitely less than that in solids (Fig. 34). Thus, the liquid state represents an intermediate state between solids and gases. Liquids are neither completely disordered (like gases) nor completely ordered (like solids). The partial order and partial disorder make the liquid state more complicated.

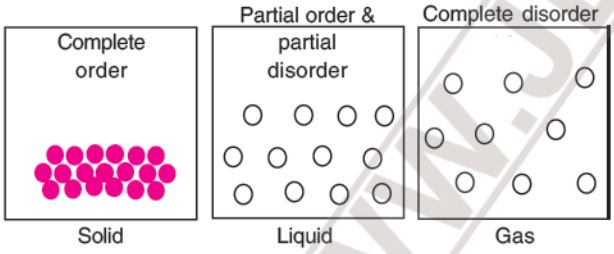

Fig. 34. Liquid state : an intermediate between solid state (complete order) and gaseous state (complete disorder).

KINETIC MOLECULAR MODEL FOR LIQUIDS

In terms of kinetic molecular model, the nature of the liquid state is described as follows :

(*i*) Liquids are composed of molecules.

(*ii*) The molecules of liquids are held together by appreciable intermolecular forces.

(*iii*) Due to weak intermolecular forces, the molecules are in constant random motion.

(*iv*) The average kinetic energy of molecules in a given sample is proportional to the absolute temperature.

It may be noted that the nature and magnitude of intermolecular forces decide the structure of a liquid and also its characteristic properties. Let us discuss the important properties of liquids with special reference to vapour pressure, viscosity, surface tension, etc.

PROPERTIES OF LIQUIDS

The important properties of liquids are discussed below:

1. Volume

Unlike gases, liquids have a definite volume. Though they take the shape of the container, they maintain their volume. In liquids, the intermolecular forces are strong and therefore, they do not expand to occupy all the space available (as gases do). Therefore, a given mass of a liquid has fixed volume.

2. Density

The molecules of liquids are more closely packed than gases. The densities of liquids are more than the densities of gases. It has been found that the densities of liquids are about 1000 times greater than the densities of gases under similar conditions.

The higher densities of liquids than gases are due to the fact that molecules of liquids are more closely packed than gases. In general, the density of the liquids decreases with increase in temperature.

3. Compressibility

Liquids are much less compressible than gases. This is due to the fact that in comparison to gases, very little space is free in the case of liquids. Moreover, the repulsive forces between molecules prevent the compressibility of liquids. Therefore, large pressure is needed to reduce the volume of a liquid to a significant extent.

4. Diffusion

Like gases, liquids also diffuse but they diffuse slowly than gases. In the liquid state, the molecules are quite close to each other. Therefore, a molecule of the liquid has to undergo a number of collisions with the neighbouring molecules. Thus, there is more obstruction for the movement of the molecules of a liquid. As a result, the diffusion takes place slowly. In contrast, in gases, there is very less obstruction to the moving molecules because of large empty spaces available for their movement.

Moreover, in liquids there are forces of attraction between individual molecules which tend to hold the molecules together. In other words, *this slows down the process of diffusion*.

5. Evaporation

An important property of liquids is their tendency to evaporate. Though the molecules of liquids are held

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together by attractive forces, yet they have a tendency to escape, which is known as evaporation. Thus, **evaporation** is

the process of conversion of a liquid into its vapours at room temperature.

We know that when a liquid is placed in open vessel, it gradually evaporates and is converted into its vapours. For example, if we take some ether in a beaker, within a few minutes, the whole of it will evaporate. The process of evaporation can be explained on the basis of kinetic molecular theory as given below:

According to kinetic theory of liquids, all the molecules in liquid state do not have the same speed. The different molecules in a liquid have different speeds and therefore, have different kinetic energies. The distribution of molecular kinetic energies in a liquid is shown in Fig. 35. There is a certain fraction of the molecules which have very high kinetic energies. These molecules can readily overcome the attractive forces in the liquid and escape from the liquid surface into vapours. This process of escaping of molecules from liquid to vapour state is called evaporation.

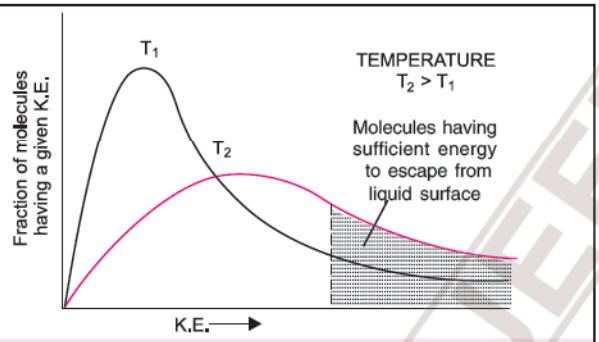

Fig. 35. Distribution of molecular kinetic energies in a liquid at two temperatures.

Cooling caused by evaporation. It may be noted that during the process of evaporation, cooling is always caused. This can be explained as :

During evaporation the molecules of higher kinetic energy escape. The slow-moving molecules are left behind and, therefore, the average kinetic energy of the molecules left in the liquid state is lowered, assuming that no heat is supplied from some outside source. The lowering of the average kinetic energy results in a temperature drop in the liquid.

Factors on which Rate of Evaporation depends

Rate of evaporation depends upon the following factors :

(*i*) Temperature. The rate of evaporation increases as the temperature of a liquid is increased. For example, a glass of hot water evaporates more rapidly than glass of cold water. As clear from Fig. 33, the distribution of molecular kinetic energies curve shifts towards right and the number of molecules having higher kinetic energies become more. Therefore, the rate of evaporation increases.

(*ii*) Strength of intermolecular forces. The ease of evaporation of a liquid is related to the strength of the attractive forces between the molecules in the liquid. For example, ether evaporates more rapidly than ethyl alcohol while ethyl alcohol evaporates quicker than water. This is because the intermolecular attractive forces in these liquids are in the order.

ether < ethyl alcohol < water

(*iii*) Surface area. The greater surface area to which the liquid is exposed, the greater is the rate of evaporation. This is because greater area helps in escaping a large number of molecules from the surface.

6. Enthalpy of vaporisation

The amount of heat required to evaporate 1 mole of a given liquid at its boiling point is known as the **enthalpy of evaporation** or **enthalpy of vaporisation.** For example, when one mole of water is completely vaporised at 100°C, it absorbs 40.6 kJ of energy.

This may be written as :

$$H_2O(l) + 40.6\ kJ \longrightarrow H_2O(g)$$

Thus, the molar enthalpy of vaporisation of water is 40.6 kJ. The enthalpy of vaporisation depends upon the strength of attractive forces between the molecules of a liquid. For example, the enthalpy of vaporisation of water at 100°C is 40.6 kJ mol^{-1}, enthalpy of vaporisation of benzene at 80°C is 30.8 kJ mol^{-1} and that of ethyl alcohol at 78°C is 39.2 kJ mol^{-1}. The relatively high molar enthalpy of vaporisation of water suggests strong attractive forces in liquid water.

7. Vapour pressure

As already discussed, if a liquid is placed in an open vessel, the molecules escape from the liquid to the atmosphere. On the other hand, if a liquid is allowed to evaporate in a closed vessel (Fig. 36), the molecules escaping from the liquid surface do not leave the container. These are collected in the vapour state above the surface of the liquid. Due to vaporisation, liquid changes into vapours and level of liquid decreases. After some time, the level of liquid does not change further and becomes constant. This behaviour of liquid can be easily understood.

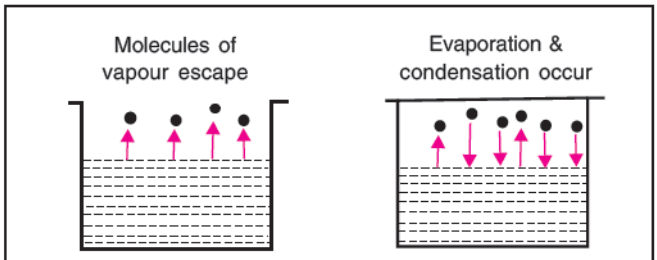

Fig. 36. Evaporation in an open vessel and in a closed vessel.

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Initially, the system contains only liquid and the space above the liquid is completely evacuated [Fig. 37 (*a*)]. As evaporation starts, the molecules from the surface of liquid escape in the vapour state and therefore, the level of liquid falls [Fig. 37 (*b*)]. The molecules which escape from the surface of the liquid get confined to a limited space above the liquid. These molecules move randomly in all directions and collide with one another, with the walls of the container and with the liquid surface. During this, some slow-moving molecules colliding with the surface of the liquid may be recaptured by the intermolecular attraction and get converted into liquid. This process is called **condensation.** In the initial stages, the rate of evaporation is more than the rate of condensation [Fig. 37 (*b*)], because only small number of molecules are present in the vapour state. Thereafter, the rate of condensation gradually increases as the number of molecules in the vapour phase increases.

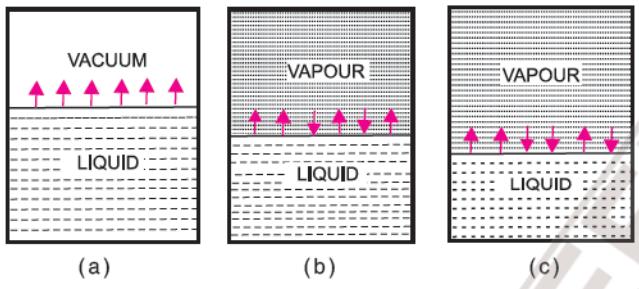

Fig. 37. Attainment of equilibrium in evaporation of a liquid.

Finally, a stage is reached when the rate of evaporation becomes equal to the rate of condensation. In such a state, the system is not at rest though there is no change in the system because the amount of liquid level in the vessel does not change. This does not mean that evaporation has stopped. In fact, the number of molecules which escape from the liquid to the vapour phase (due to evaporation) becomes equal to the number of molecules which return to the liquid from the vapour phase. Therefore, the amount of liquid becomes constant [Fig. 37 (*c*)]. This state is known as ***dynamic equilibrium***. This is the condition when two opposing processes occur at equal rate.

The molecules in the vapour phase exert pressure. As the evaporation reaches the equilibrium state, the concentration of the molecules in the vapour state becomes constant. The pressure exerted by the molecules in the gaseous phase in equilibrium with its liquid is called equilibrium vapour pressure of the liquid. But more commonly, it is called vapour pressure. Thus, **vapour pressure** may be defined as

the pressure exerted by the vapours in equilibrium with its liquid at a given temperature.

This is also called **saturated vapour pressure.** The vapour pressure is a characteristic property of a liquid at a given temperature. It does not depend upon the amount of the liquid or the vapour phase. The magnitude of vapour pressure depends upon the following two factors :

(*i*) **Nature of liquid.** *The vapour pressure of a liquid depends upon the nature of the liquid.* When intermolecular forces are weak, the molecules tend to escape readily and therefore, the equilibrium vapour pressure is high. Therefore, the vapour pressure of liquids provide an indication of the magnitude of intermolecular forces. As mentioned previously, ether and alcohol evaporate faster than water. Hence, we would expect ether and alcohol to have higher vapour pressure than water at a given temperature. This is actually so. The higher vapour pressure of ether and alcohol as compared to water is due to the fact that there are weaker attractive forces in ether and alcohol as compared to water.

(*ii*) **Temperature of liquid.** *The vapour pressure of a liquid increases with increasing temperature*. As the temperature increases, the fraction of molecules having larger kinetic energy increases. Therefore, more molecules escape from the surface of the liquid. Therefore, concentration of molecules in the vapour phase will increase. Hence, vapour pressure of the liquid increases.

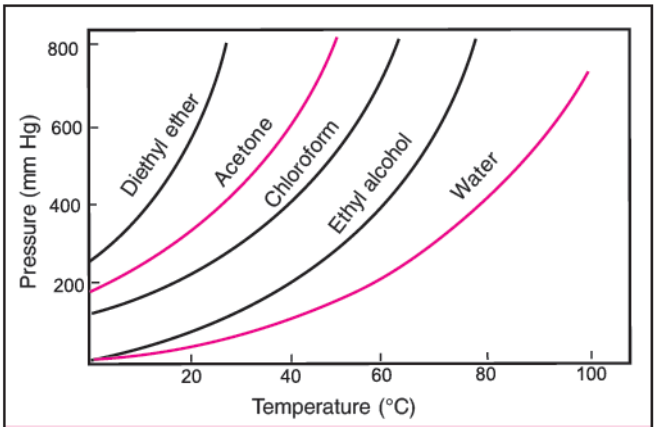

Fig. 38. Temperature dependence of vapour pressure of liquids.

8. Boiling

We have learnt that the vapour pressure of a liquid increases with rise in temperature. Ultimately, a stage is reached when the vapour pressure of the liquid becomes equal to atmospheric prossure. At this point, the vapours formed within the liquid can easily rise through the liquid in the form of bubbles and escape. This phenomenon is known as boiling and the

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temperature at which this occurs is known as **boiling point**. Therefore, **boiling point** is the

temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure.

The boiling point, therefore, depends upon the atmospheric pressure. At high altitudes, atmospheric pressure is low and therefore liquids at high altitudes boil at lower temperature in comparison to sea level. *Thus, at high altitudes like Shimla water boils at a much lower temperature than in the plains like Jalandhar because atmospheric pressure is less at high altitudes.* Since water boils at low temperature on hills, the pressure cooker is generally used for cooking food. In hospitals, surgical instruments are sterilized in autoclaves in which boiling point of water is increased by increasing the pressure above the atmospheric pressure by using a weight covering the vent.

Generally, boiling points for most of the liquids are specified as *normal boiling points. The* ***normal boiling point of a liquid*** *is the temperature at which the vapour pressure of the liquid becomes equal to one atmospheric pressure*.

If pressure is 1 bar, then the boiling point is called **standard boiling point** of liquid. Standard boiling point of a liquid is slightly lower than the normal boiling point because 1 bar pressure is slightly less than 1 atm pressure. Its value can be determined from the vapour pressure temperature curves. The broken horizontal line corresponds to 1 atm (760 mm Hg). The temperature at which the vapour pressure curve crosses the horizonal line is the normal boiling point of that liquid.

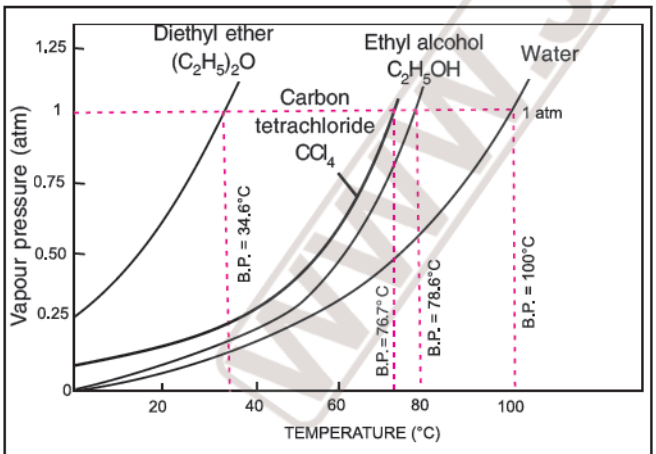

Fig. 39. Vapour pressure temperature curves for water, ethyl alcohol, carbon tetrachloride and diethyl ether and their boiling points.

For example, as shown in Fig. 39, the vapour pressure -temperature curve for water crosses at 100°C and therefore, the normal boiling point of water is 100°C (373K). The standard boiling point of water is 99.6°C (372. 6 K).

Effect of change in External Pressure on the Boiling Point

A liquid may be made to boil at any desired temperature by changing the external pressure. For example, a liquid may be made to boil at a lower temperature than the normal boiling point by reducing the external pressure or it may be made to boil at higher temperature by increasing the pressure. It is observed that some substances decompose at their normal boiling points and therefore, they cannot be heated upto their boiling points. They are made to boil at reduced pressure. This principle is used in purifying less stable liquids by distillation under reduced pressure. This process is called **vacuum distillation**.

It may be noted that once the boiling starts, the temperature of the liquid remains constant, even though heating is continued, until the whole of the liquid has vaporised. A curious question comes to our mind. **"Why does the temperature of the boiling liquid remains constant even though heating is continued ?"** This can be explained as follows :

When a liquid is heated, the heat supplied is consumed to pull the liquid molecules apart against strong attractive forces which hold them together in the liquid form. Thus, the heat energy goes to compensate the loss of energy due to escaping molecules which have to overcome the attractive forces between the molecules of the liquid. As a result, there is no change in the average kinetic energy of the molecules remaining in the boiling liquid. Since, the average kinetic energy is proportional to the temperature ($\frac{1}{2}mv^2 \propto T$), therefore, the temperature of the liquid does not change till the whole of liquid has been converted into the vapour state.

Boiling does not occur when a liquid is heated in a closed container. On heating continuously, vapour pressure increases. At first, a clear boundary becomes visible between liquid and vapour phase because liquid is more dense than vapour. But as the temperature rises, more and more molecules of liquid go to vapour phase. As a result, density of vapour increases. At the same time, liquid becomes less dense and expands because molecules move apart. When density of liquid and vapours becomes the same, the clear boundary between liquid and vapours disappears. This temperature is called **critical temperature.** We have already learnt about it.

Although boiling and evaporation are similar processes, yet they differ in many respects. The main

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points of **difference between evaporation and boiling** are given below :

Evaporation	Boiling
1. Evaporation process takes place spontaneously at all temperatures.	Boiling takes place only at definite temperature (boiling point) at which the vapour pressure of the liquid is equal to the atmospheric pressure.
2. Evaporation takes palce only at the surface of the liquid	Boiling takes place even below the surface of the liquid in the form of bubbles.

9. Surface tension

Liquids exhibit an interesting property known as surface tension. It is also related to the intermolecular forces in the liquid. As mentioned previously, the molecules in liquids are held closely and hence attract each other. A molecule in the bulk of the liquid is attracted equally on all sides so that the net attractive pull on the molecule is zero (Fig. 40). However, a molecule which lies at the surface (known as surface molecule) is subjected only to the attractive forces of the molecules below it. This is because there are no molecules above it. Therefore, surface molecules experience a resultant downward attractive force from within the liquid. This creates an imbalance of forces at the surface. In other words, the liquid surface is under tension due to imbalanced forces. This effect is called **surface tension.** As a result of this, the molecules at the surface are pulled inwards and tend to make the surface area of the liquid as small as possible. Whenever, we want to increase the surface of the liquid, then the molecules from the body of the liquid state have to be brought to the surface of the liquid and this requires work to overcome the attractive forces.

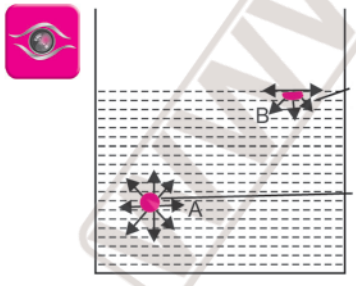

Fig. 40. Forces acting on a molecule in the bulk of the liquid and at the surface.

The energy required to increase the surface area of the liquid by one unit is called **surface energy. Surface tension** is also defined as

force per unit length acting perpendicular to the tangential line drawn on the surface of the liquid.

It is represented by the Greak letter γ (gamma).

Units of surface tension

The units of surface tension are force per unit length, *i.e.* dyne cm^{-1}. In SI system, the units are N m^{-1}. For example, the surface tension of water is 72.75×10^{-3} N m^{-1} and that of mercury is 47.5×10^{-2} N m^{-1}.

Due to the surface tension, the liquid drops have nearly spherical shape because sphere has minimum surface area for the given volume of liquid. You must have noticed that when a mercury thermometer breaks, mercury spreads in small spherical drops. It is also responsible for rise or fall of a liquid in a capillary tube.

Effect of temperature. *Surface tension decreases with rise in temperature.* The decrease of surface tension with increase of temperature is because of the fact that the kinetic energy (or speeds) of the molecules increases. As a result, the intermolecular forces decrease and therefore, surface tension also decreases. For example, the clothes are washed more efficiently in hot water than in cold water due to decreased surface tension in hot water.

Surface tension and nature of liquid. Since surface tension of a liquid is due to intermolecular attractive forces, therefore, the magnitude of surface tension is a measure of intermolecular attractive forces. When the attractive forces between the molecules are large, the surface tension is large.

Consequences of Surface Tension

The following two important phenomena are due to surface tension :

(*i*) Spherical shape of drops. The liquid drops have nearly spherical shapes. We have learnt that surface tension tries to decrease the surface area of a liquid to the minimum. Since the sphere has minimum surface area for the given volume of liquid, therefore, the liquid tries to adopt spherical shape [Fig. 41]. That is why mercury drops are spherical in shape. This is also the reason that sharp glass edges are heated for making them smooth. On heating, the glass melts and the surface of liquid tends to take rounded shape at the edges. This makes the edges smooth and is called **fire polishing of glass.**

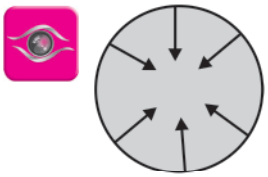

Fig. 41. Inward pull of surface tension makes a drop spherical.

It is the surface tension which gives stretching property to the surface of a liquid. On a flat surface, droplets are slightly flattened due to gravity. However, in gravity free environment droplets are perfectly

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spherical. It may be noted that water drop in vacuum is perfectly spherical. The shape of the water drop is distorted due to action of gravity.

***(ii)* Capillary action.** When one end of a capillary tube is put into a liquid that wets glass [Fig. 42], the liquid rises into the capillary tube to a certain height and then stops. The rise of a liquid in capillary is called **capillary action.** The rise of liquid in a capillary is due to the inward pull of surface tension acting on the surface which pushes the liquid into the capillary tube. This phenomenon is very important. For example,

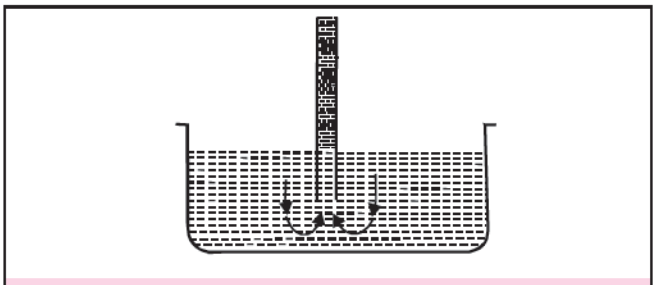


Fig. 42. Rise of a liquid in a capillary tube.

water below the surface of the earth rises to the plants through the roots, oil rises into the wick of an oil lamp, ink rises in a blotting paper, are examples of capillary action.

***(iii)* Liquid wets the things**. Liquids wet the things because these spread across their surfaces as they flow. Moist soil grains are pulled together because surface area of thin water film is decreased.

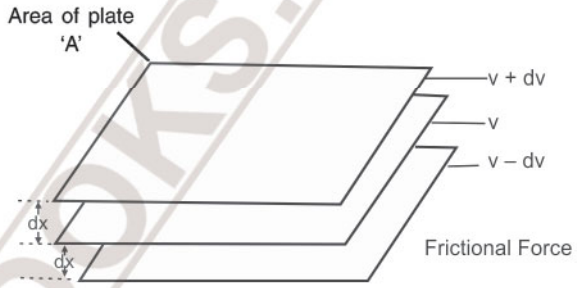
10. Viscosity.

It is a common observation that certain liquids flow faster than others. For example, water and kerosene oil flow rapidly while honey and castor oil flow slowly. Thus,

viscosity is internal resistance to flow in liquids which arises due to the internal friction between layers of liquid as they slip past one another while liquid flows.

Strong intermolecular forces between molecules hold them together strongly and therefore, resist movement of layers past one another.

The cause of different rates of flow of liquids may be easily understood by considering flow of liquid on a glass plate. The liquid may be imagined to consist of a large number of molecular layers arranged one above the other. The molecular layer which is in contact with the glass plate remains almost stationary. The second layer moves slightly faster than the first layer and the third layer moves still faster. Thus in a liquid, each successive layer moves with gradually increasing speed. Therefore, the different layers in a liquid move over one another with different speeds in the direction of the flow of the liquid. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called **laminar flow.** However, due to intermolecular forces, there is resistance of one layer to the other layer. For example, if we select a layer, the layer immediately below it tries to retard its flow (velocity) while the one above it tries to accelerate the flow. If the velocity of the layer at a distance dx is changed by a value dv, then velocity gradient is given by the amount $\frac{dv}{dx}$. A force is required to maintain the flow of layers. The force required to maintain the flow in the three layers is directly proportional to the area of contact and velocity gradient. *i.e.,*



Force, $f \propto A$

$\propto \frac{dv}{dx}$

where A is the area of contact and $\frac{dv}{dx}$ is the velocity gradient. *i.e.* the change in velocity with distance

or $$F = \eta A \frac{dv}{dx}$$

where η is a proportionality constant and is called the coefficient of viscosity.

Now, $F = \eta$ when $A = 1$ and $\frac{dv}{dx} = 1$

i.e., Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus, **viscosity coefficient** may be defined as

the force of friction required to maintain unit velocity gradient between two parallel layers of unit area of contact.

The viscosities of liquids are compared in terms of coefficient of viscosity. This is also defined as *the tangential force per unit area required to maintain a unit difference in velocities.*

Units of viscosity. As we have learnt,

$$f = \eta A \frac{dv}{dx} \text{ or } \eta = \frac{f}{A}\frac{dx}{dv}$$

or $$\eta = \frac{\text{dynes} \times \text{cm}}{\text{cm}^2 \times \text{cm/sec}}$$

or $$= \text{dynes cm}^{-2} \text{ sec}$$

Thus, the units of viscosity are dynes cm^{-2} sec. This quantity is also called **poise**, P, after the name of great scientist Jean Louise Poiseuille, in the field of viscosity.

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Now, $f = m \times a$ so that

$$\eta = \frac{m \times a \times dx}{A \times dv}$$

$$= \frac{g \times \text{cm s}^{-2} \times \text{cm}}{\text{cm}^2 \times \text{cm s}^{-1}} = g \text{ cm}^{-1} s^{-1}$$

$\therefore$ **1 poise = 1 *g* cm^{-1} s^{-1}**

Sometimes, the smaller units centipoise (cP = 10^{-2}P) and millipoise (mP = 10^{-3} P) are used.

In SI system, the units of viscosity are **Nm^{-2}** *s* or **Pa.s** (where Pa is pascal) or kg m^{-1}s^{-1}.

$$\eta = \frac{f \times dx}{A \times dv} = \frac{\text{N} \times \text{m}}{\text{m}^2 \times \text{ms}^{-1}} = \textbf{Nm}^{-2}\textbf{s}$$

or $= \textbf{Pa.s or kgm}^{-1}\textbf{s}^{-1}$

Commonly used unit poise is one tenth of the SI unit, *i.e.*

$$1\text{P} = 0.1 \text{ N m}^{-2} \text{ s}.$$

Viscosity and nature of liquid. The viscosity is also related to the intermolecular forces in the liquid. If the intermolecular forces are large, the viscosity will be high. For example, water has higher viscosity than methyl alcohol because intermolecular forces in water are more than in methyl alcohol.

Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity to liquids. Greater the viscosity, the more slowly the liquid flows. A liquid like water that flows easily has low viscosity while a liquid like heavy engine oil which flows slowly is said to have a high viscosity. Glass is extremely viscous liquid. It is so viscous that many of its properties resemble solids. However, its property of flow can be experienced by measuring the thickness of window panes of old buildings. These become thicker at the bottom than at the top showing the property that glass flows.

Effect of temperature. *Viscosity of a liquid decreases with rise in temperature.* With the increase in temperature, the average kinetic energy increases and the intermolecular forces can be easily overcome. Therefore, the liquid starts moving faster. It has been observed that the decrease in viscosity is about 2% per degree rise of temperature.

SOLVED EXAMPLES

Example 55.

The melting point is a rough measure of the attractive forces in solids. Arrange the following solids in the order of increasing strength of attractive forces.

	m.p. (K)
Naphthalene	*353*
Sodium fluoride	*1272*
Water (ice)	*273*
Phosphorus	*317*
Zinc iodide	*719*

Solution: The order of increasing strength of attractive forces is :

Water, phosphorus, naphthalene, zinc iodide, sodium fluoride.

Example 56.

Which of the liquids in each of the following pairs has a higher vapour pressure ?

(a) alcohol, glycerine

(b) mercury, water

(c) petrol, kerosene

Solution: Liquids having higher vapour pressure.

(*a*) alcohol

(*b*) water

(*c*) petrol.

Practice Problems

52. Which of the following statements are correct ?

(*a*) With rise in temperature surface tension of a liquid increases.

(*b*) The rise of a liquid in a capillary is due to the phenomenon of diffusion.

(*c*) The boiling point of water is lower in Shimla than in Jalandhar.

(*d*) The viscosity of a liquid is generally more than that of a gas.

53. The heats of vaporisation of water, ethyl alcohol and carbon disulphide are 40.6, 38.6 and 26.8 kJ mol^{-1} respectively. Arrange these in the decreasing order of intermolecular forces.

54. Which one, in each of the following pairs is more viscous ?

(*a*) coconut oil, castor oil

(*b*) glycerine, kerosene

(*c*) soft drink, aerated water

Answers to Practice Problems

52. (*c*), (*d*)

53. Water > ethyl alcohol > carbon disulphide

54. (*a*) castor oil , (*b*) Glycerine (*c*) Soft drink

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add on

Conceptual Questions 2

CONCEPTUAL QA

Q. 1. The Van der Waals constants for two gases A and B are as follows :

Gas	a (atm L^2 mol^{-2})	b (L mol^{-1})
A	1.63	0.0326
B	3.72	0.0521

which of these

(*i*) is more easily liquefied ? (*ii*) has larger molecular size ?

Ans. (*i*) Greater the value of 'a' more easily the gas is liquefied. Hence gas B is more easily liquefied.

(*ii*) Larger the value of 'b', larger is its molecular size. Therefore, B has larger molecular size.

Q. 2. What property of molecules of real gases is indicated by Van der Waals constant 'a' ?

Ans. Intermolecular attraction.

Q. 3. Which two postulates of the kinetic molecular theory are only approximations when applied to real gases ?

Ans. (*i*) Intermolecular forces between molecules are negligible.

(*ii*) Molecules of a gas have negligible volumes.

Q. 4. What is triple point of a substance ?

Ans. It is the point at which solid, liquid and vapour of a substance are in equilibrium with each other. For example, triple point of water is the temperature at which ice, water and its vapour coexist.

Q. 5. Why has urea a sharp melting point but glass does not have sharp melting point ?

Ans. Urea is a crystalline substance and therefore, has a sharp melting point. On the other hand, glass is an amorphous solid and therefore, does not have sharp melting point.

Q. 6. At a particular temperature, why vapour pressure of acetone is less than that of ether ?

Ans. This is because intermolecular forces in acetone are more than those present in ether.

Q. 7. Explain why water would completely fill a fine capillary tube which is open at both ends when one end is immersed in water.

Ans. The surface tension pulls the water into the capillary. In a fine capillary, the surface tension is large enough to overcome the attraction of gravity on water.

Q. 8. Why falling liquid drops are spherical ?

Ans. This is due to surface tension of liquids. Due to surface tension, the molecules of a liquid, try to make surface area to be minimum and for a given volume, sphere has the minimum surface area. Therefore, the falling liquid drops are spherical.

Q. 9. Explain why evaporation leads to cooling of the liquid.

Ans. This is due to the reason that the molecules which undergo evaporation are high energy molecules and therefore, the kinetic energy of the remaining molecules becomes less. Since the remaining molecules have lower average kinetic energy, their temperatures become low.

Q. 10. Out of NH_3 and N_2, which will have (*i*) larger value of a and (*ii*) larger value of b ?

Ans. (*i*) NH_3 will have larger value of a because of hydrogen bonding.

(*ii*) N_2 should have larger value of b because of larger molecular size.

Q. 11. What would have happened of the gas pressure if the molecular collisions were not elastic ?

Ans. The gas pressure would have gradually become zero.

Q. 12. Why are the gases helium and hydrogen not liquefied at room temperature by applying very high pressure ?

Ans. Because their critical temperature is lower than room temperature. Gases cannot be liquefied above the critical temperature by applying even very high pressure.

Q. 13. Name the liquid with higher vapour pressure in the following pairs :

(*a*) Petrol, kerosene (*b*) Water, mercury (*c*) Alcohol, glycerine.

Ans. (*a*) Petrol (*b*) Water (*c*) Alcohol

Q. 14. What is Boyle temperature ?

Ans. The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called Boyle temperature.

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CONCEPTUAL QA

Q. 15. Name the intermolecular forces between

(*i*) Cl_2 and CBr_4 (*ii*) SiH_4 molecules (*iii*) He atoms in liquid He

(*iv*) HCl molecules in liquid HCl (*v*) He and a polar molecule (*vi*) Water molecules

Ans. (*i*) Dispersion forces (*ii*) Dispersion forces

(*iii*) Dispersion forces (*iv*) Dipole-dipole interactions

(*v*) dipole-induced dipole (*vi*) Hydrogen bonding

Q. 16. Why does a liquid boils at a lower temperature at the top of a mountain than at sea level ?

Ans. This is because pressure at the top of a mountain is low.

Q.17. How is compressibility factor expressed in terms of molar volume of a real gas and that of the ideal gas ?

Ans. $Z = \frac{V_{real}}{V_{ideal}}$

Q. 18. What is SI unit of coefficient of viscosity?

Ans. $Nm^{-2}\,s$ or $kg\,m^{-1}\,s^{-1}$.

Q.19. Name two intermolecular forces that exist between HF molecules in liquid state.

Ans. (*i*) Dipole–dipole interactions (*ii*) Hydrogen bonding.

Q.20. For gases like H_2 and He which show only positive deviation from ideal behaviour, the compressibility factor is greater than 1. Is the statement true or false ?

Ans. True.

Advanced Level PROBLEMS *Accelerate Your Potential (for JEE Advance)*

Problem 11. Two flaska A and B have equal volume. Flask A contains H_2 and is maintained at 300 K while flask B contains an equal mass of CH_4 gas and is maintained at 600 K.

(*i*) Which flask contains a greater number of molecules? How many times more?

(*ii*) In which flask is the pressure greater? How many times greater?

(*iii*) In which flask will the molecules move faster?

(*iv*) In which flask will the number of collisions with the wall greater?

Solution (*i*) Let the mass of each gas present in two flasks = 1 g

Molar mass of H_2 = 2, Molar mass of CH_4 = 16

Moles of hydrogen in flask A = $\frac{1}{2}$

Moles of CH_4 in flask B = $\frac{1}{16}$

Since the number of moles of H_2 is more than those of CH_4, flask A contains greater number of molecules.

Ratio of moles of H_2 and CH_4 = $\frac{\frac{1}{2}}{\frac{1}{16}} = 8$.

Since moles are directly proportional to the number of molecules, flask A contains eight times more molecules than those present in flaks B.

(*ii*) Since flask A contains large molecules than those in flask B (both of same volume), the pressure in flask A will be greater.

$$p(H_2) = \frac{nRT}{V} = \frac{\frac{1}{2}\times R\times 300}{V}$$

$$p(CH_4) = \frac{nRT}{V} = \frac{\frac{1}{16}\times R\times 600}{V}$$

$$\frac{p(H_2)}{p(CH_4)} = \frac{1}{2}\times 300\times 16\times\frac{1}{600} = 4$$

Pressure of H_2 in flask A will be four times the pressure of CH_4 in flask B.

(*iii*) The speed of molecules can be compared in terms of root mean square speed. It is given by

$$u_{r.m.s.} = \sqrt{\frac{3RT}{M}}$$

In Flask A, $u_{r.m.s.}(H_2) = \sqrt{\frac{3\times R\times 300}{2}}$

In Flask B, $u_{r.m.s.}(CH_4) = \sqrt{\frac{3\times R\times 600}{16}}$

$$\frac{u_{r.m.s.}(H_2)}{u_{r.m.s.}(CH_4)} = \sqrt{\frac{3\times 300}{2}}\times\sqrt{\frac{16}{3\times 600}} = 2$$

The molecules of H_2 in flask A will move faster than molecules of CH_4 in flask B.

(*iv*) Since hydrogen molecules move faster than CH_4 molecules, the number of collisions in flask A will be greater.

Problem 12 The average velocity at T_1K and the most probable velocity at T_2 K of CO_2 gas is 9.0×10^4 cm s^{-1}. Calculate the values of T_1 and T_2.

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Solution Average velocity $= \sqrt{\frac{8RT}{\pi M}}$

Most probable velocity $= \sqrt{\frac{2RT}{M}}$

Average velocity at T_1 K = Most probable velocity at T_2 K

$= 9.0 \times 10^4$ cm s^{-1}

$R = 8.314 \times 10^7$ ergs K^{-1} mol^{-1}, M = 44

Average velocity at T_1 K

$$\sqrt{\frac{8\times8.314\times10^7\times T_1}{3.143\times44}} = 9.0\times10^4$$

$$T_1 = \frac{81\times10^8\times3.143\times44}{8\times8.314\times10^7} = 1682.5 \text{ K}$$

Similarly, $\sqrt{\frac{2\times8.314\times10^7\times T_2}{44}} = 9.0\times10^4$

$$T_2 = \frac{81\times10^8\times44}{2\times8.314\times10^7} = \textbf{2143 K.}$$

Problem 13 Using van der Waals equation, calculate the constant '*a*' when two moles of a gas confined in a 4L flask exerts a pressure of 11.0 atmospheres at a temperature of 300 K. The value of *b* is 0.05 L mol^{-1}.

Solution Van der Waals equation is

$$\left(p+\frac{an^2}{V^2}\right)(V-nb) = nRT$$

$n = 2$ mol, V = 4L, $p = 11$ atm, T = 300 K,

$b = 0.05$ L mol^{-1}

Substituting the values

$$\left(11+\frac{a\times4}{16}\right)(4-2\times0.05) = 2\times0.082\times300$$

$$\frac{176+4a}{16}\times3.9 = 49.2$$

$$(176+4a)\,3.9 = 49.2\times16$$

$$15.6\,a = 787.2-686.4$$

$$a = 6.4615 \text{ atm } L^2 \text{ mol}^{-2}$$

Problem 14 The compressibility factor for one mole of a van dar Waals gas at 0°C and 100 atm pressure is found to be 0.5. Assume that the volume of gas molecules is negligible, calculate the van der Waals constant '*a*'.

Solution Compressibility factor,

$$Z = \frac{pV}{RT}$$

$$0.5 = \frac{100\times V}{0.082\times273}$$

$$\therefore \quad V = \frac{0.5\times0.082\times273}{100} = 0.1119\text{L}$$

If volume of molecules is negligible *i.e.* *b* is negligible van der Waals equation:

$$\left(p+\frac{a}{V^2}\right)(V) = RT$$

or $pV = RT - a/V$

or $a = RTV - pV^2$

$= (0.082\times273\times0.1119) - (100\times0.1119\times0.1119)$

$= \textbf{1.253 atm L}^2 \textbf{ mol}^{-2}$.

Solution File

Hints & Solutions for Practice Problems

1. $V_1 = 5L$, $p_1 = \frac{750}{760}$ atm

$V_2 = 1L$, $p_2 = \frac{p_1V_1}{V_2} = \frac{(750/760)\text{atm}\times5L}{1L} = \textbf{4.93 atm}$

2. $V_1 = 175$ L, $p_1 = 1$ bar

$V_2 = ?$, $p_2 = 0.80$ bar

Applying Boyle's law,

$p_1V_1 = p_2V_2$ or $V_2 = \frac{p_1V_1}{p_2}$

$$V_2 = \frac{(1\text{ bar})\times(175\text{ L})}{(0.80\text{ bar})} = \textbf{218.75L.}$$

3. Since temperature is constant, therefore, by applying Boyle's law,

$$V_2 = \frac{p_1V_1}{p_2} \text{ or } V_2 = \frac{0.867\times10^5\text{Pa}\times(2L)}{(10^5\text{Pa})} = \textbf{1.734 L.}$$

4. Applying Boyle's law,

$$V_2 = \frac{p_1V_1}{p_2} \text{ or } V_2 = \frac{(0.720\text{ bar})\,(200\text{mL})}{(0.900\text{ bar})} = \textbf{160 mL.}$$

5. On opening the stop cock, the same number of moles of the gas occupy a volume of (V + 0.5) litre at the same temperature. Applying Boyle's law.

$p_1V_1 = p_2V_2$; 1 atm = 101.325 kPa = 101325 Pa

$101325\times V = 7.58\times10^4\,(V+0.5)$

$101325V - 75800V = 37900$

$25525\,V = 37900$ or $V = \frac{37900}{25525} = \textbf{1.48 L}$

6. According to Boyle's law, at constant temperature,

$p_1V_1 = p_2V_2$

if $p_1 = 1.2$ bar, $V_1 = 4.5$ dm^3

$p_2 = 1.8$ bar, $V_2 = ?$

$1.2\text{ bar}\times4.5\text{ dm}^3 = 1.8\text{ bar}\times V_2$

$$V_2 = \frac{1.2\text{ bar}\times4.5\text{ dm}^3}{1.8\text{ bar}} = 3.0\text{ dm}^3$$

Change in volume = 4.5 – 3.0 = **1.5 dm^3.**

7. Since pressure is constant, therefore, by applying Charles' law.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ or } V_2 = \frac{V_1T_2}{T_1}$$

$T_1 = 273 - 10 = 263$ K,

$T_2 = 273 + 10 = 283$ K

$$V_2 = \frac{(0.5\text{ dm}^3)\times283\text{K}}{263\text{K}} = \textbf{0.538 dm}^3$$

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Solution File

8. $V_1 = 800$ mL, $T_1 = 273 + 22 = 295$ K

Increase in volume $= \frac{800 \times 20}{100} = 160$ mL

$\therefore$ $V_2 = 800 + 160 = 960$ mL, $T_2 = ?$

Since pressure remains constant, therefore, by applying Charles' law,

$$T_2 = \frac{V_2 T_1}{V_1} = \frac{(960 \text{ mL}) \times (295 \text{ K})}{800 \text{ mL}} = 354 \text{ K}$$

or $T_2 = 354 - 273 = \mathbf{81°C.}$

9. $V_1 = V$ (say) $T_1 = 273 + 0 = 273$ K

$V_2 = \frac{V}{2}$ $T_2 = ?$

Since pressure remains constant, therefore, by applying Charles' law,

$$T_2 = \frac{V_2 T_1}{V_1} = \frac{(V/2) \times (273 \text{ K})}{V} = 136.5 \text{ K}$$

or $136.5 - 273 = -\mathbf{136.5°C.}$

10. Let us first calculate the final volume,

$V_2 = ?$

$$V_2 = \frac{V_1 T_2}{T_1}$$

$\therefore$ $$V_2 = \frac{10 \times 250}{400} = 6.25 \text{ L}$$

Final volume of the air = 6.25 L

Volume of air expelled = $10 - 6.25 = \mathbf{3.75 \text{ L.}}$

11. Avogadro number = 6.022×10^{23}

10^{10} grains are distributed in = 1 sec

6.022×10^{23} grains would be distribtued in

$$= \frac{6.022 \times 10^{23}}{10^{10}} \textbf{ sec}$$

$$= \frac{6.022 \times 10^{23}}{10^{10} \times 3600 \times 24 \times 365}$$

$= \mathbf{1.9096 \times 10^6 \text{ years.}}$

12. $V_1 = 431$ *ml* $V_2 = ?$

$p_1 = 1$ bar $p_2 = 1.05$ bar

$T_1 = 273$ K $T_2 = 273 + 35 = 308$ K

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \quad \text{or} \quad V_2 = \frac{p_1 V_1 T_2}{p_2 T_1}$$

$$V_2 = \frac{(1 \text{ bar}) \times (431 \text{mL}) \times (308 \text{K})}{(1.05 \text{ bar}) \times (273 \text{ K})} = \mathbf{463.1} \text{ mL}$$

13. Mass = 10 g, $n = \frac{10}{32}$ mol, V = 5 dm^3, T = 273 + 26 = 299 K

$pV = nRT$,

$$\therefore \quad p = \frac{\left(\frac{10}{32} \text{mol}\right) \times \left(0.08314 \text{ dm}^3 \text{ bar K}^{-1}\text{mol}^{-1}\right) \times (299 \text{ K})}{5 \text{ dm}^3}$$

$= \mathbf{1.55 \text{ bar.}}$

14. Capacity of life jacket = Vol. of CO_2 required,

V = 4 L

Pressure, $p = 1$ atm Temperature, T = 273 K

Density of liquid CO_2, $d = 0.8$ g cm^{-3}

Molar mass of CO_2, M = 44

Mass of CO_2 can be calculated from the relation

$$pV = \frac{m}{M} RT \text{ or } m = \frac{pVM}{RT} = \frac{1 \times 4 \times 44}{0.082 \times 273} = 7.86 \text{ g}$$

Now, $d = \frac{m}{V}$ or $V = \frac{m}{d} = \frac{7.86 \text{g}}{0.8 \text{ g cm}^{-3}} = \mathbf{9.82 \text{ cm}^3.}$

15. $$V_2 = \frac{p_1 V_1 T_2}{p_2 T_1} = \frac{(1 \text{ bar}) \times (150 \text{ mL}) \times (293\text{K})}{(0.96 \text{ bar}) \times 273}$$

$= 167.7$ mL

Change in volume = $167.7 - 150 = \mathbf{17.7 \text{ mL.}}$

16. V = 0.45 L, T = 273 + 67 = 340 K, $p = 0.76$ bar

We can first calculate number of moles from ideal gas equation,

$n = \frac{pV}{RT}$, where R = 0.08314 L bar K^{-1} mol^{-1}

$$n = \frac{(0.76 \text{ bar}) \times (0.45 \text{ L})}{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1}) \times (340\text{K})} = 0.0121$$

Number of molecules = $n \times N_A = 0.0121 \times 6.023 \times 10^{23} = \mathbf{7.3 \times 10^{21}}$.

17. $d = 1.27$ g dm^{-3}, T = 273 + 50 = 323 K,

$p = 0.987 \times 10^5$ Pa = 0.974 bar

Molar mass can be calculated as

$$M = \frac{dRT}{p}$$

$$= \frac{(1.27 \text{g dm}^{-3}) \times (0.08314 \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}) \times (323\text{K})}{(0.974 \text{ bar})}$$

$= \mathbf{35.01 \text{ g mol}^{-1}.}$

18. $d \propto \frac{1}{V}$ or $\frac{d_1}{d_2} = \frac{V_2}{V_1}$ or $d_2 = d_1 \left(\frac{V_1}{V_2}\right)$

Applying combined gas law,

$$d_2 = \frac{d_1 \times T_1 \times p_2}{T_2 \times p_1}, \; p_1 = 760 \text{ torr}, \; p_2 = 800 \text{ torr}$$

$\therefore$ $$d_2 = \frac{1.43 \times 273 \times 800}{290 \times 760} = \mathbf{1.417 \text{ g/L.}}$$

19. Molecular mass of phosphorus, $M = \frac{wRT}{pV}$

$w = 0.0625$ g,

V = 34. 05 *mL* = 34.05×10^{-3} L, $p = 1.0$ bar

T = 273 + 546 = 819 K, R = 0.08314 L bar K^{-1} mol^{-1}

$$M = \frac{0.0625 \times 0.08314 \times 819}{1 \times 34.05 \times 10^{-3}} = 124.9.$$

Since atomic mass of phosphorus is 31,

No. of atoms of phosphorus in one molecule

$$= \frac{124.9}{31} = \mathbf{4.}$$

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20. Let the volume of the tank = V litres

As number of moles of gas in the cylinder before and after connecting it to the tank will be same,

Moles of N_2 before connected = Moles of N_2 after connecting to tank

$$\frac{p_1V_1}{RT_1} = \frac{p_2V_2}{RT_2}$$

$p_1 = 20.5$ bar, $p_2 = 11.2$ bar, $V_1 = 50$ litres, $V_2 = (50 + V)$ litres

$$T_1 = T_2 = T \text{ (say)}$$

$$\frac{20.5\times50}{RT} = \frac{11.2\times(50+V)}{RT}$$

$$11.2\ V = 465$$

or $$V = \frac{465}{11.2} = \mathbf{41.5\ L.}$$

21. Let the mixture contains a g of He

Mass of Ar = $18 - a$

Moles of He, $n_{He} = \frac{a}{4}$

Moles of Ar, $n_{Ar} = \frac{18-a}{40}$

$$pV = nRT = (n_{He} + n_{Ar})\,RT$$

$$1 \times 30 = \left(\frac{a}{4} + \frac{18-a}{40}\right) \times 0.0821 \times 300$$

$$\frac{a}{4} + \frac{18-a}{40} = \frac{1\times30}{0.0821\times300}$$

$$10a + 18 - a = \frac{1\times30\times40}{0.0821\times300} = 48.72$$

$$9a = 48.72 - 18 = 30.72$$

$$\therefore \quad a = 3.41 \text{ g}$$

Mass of He = 3.41 g, Mass of Ar = 18 – 3.41 = 14.59g

$$\%\ \text{He} = \frac{3.41}{18}\times100 = \mathbf{18.95},$$

$$\%\ \text{Ar} = \frac{14.59}{18}\times100 = \mathbf{81.05}$$

22.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$T_1 = 273 + 27 = 300\ K$$

$$T_2 = 273 + 477 = 750\ K$$

$$\frac{V_1}{V_2} = \frac{300}{750} = \frac{2}{5}$$

Fraction of air expelled = $1 - \frac{2}{5} = \frac{3}{5}$.

23. Volume occupied by 0.184 g of H_2 gas at 17°C and pressure, p (say) may be calculated as :

$$pV_1 = nRT = \frac{w}{M}RT$$

or $$V_1 = \frac{w}{Mp}RT = \frac{0.814\times0.0821\,(273+17)}{2p}$$

$$= \frac{2.1904}{p}$$

Volume occupied by 2.9 g of gas at 95°C at same pressure.

$$V_2 = \frac{w}{Mp}RT = \frac{2.9\times0.0821\times368}{Mp}$$

$$\frac{2.1904}{p} = \frac{2.9\times0.0821\times368}{Mp}$$

$$M = \frac{2.9\times0.0821\times368}{2.1904} = \mathbf{40\ g\ mol^{-1}.}$$

24. Volume occupied by 0.184 g of H_2 gas at 17°C and at pressure p (say) may be calculated as

$$pV_1 = nRT = \frac{w}{M}RT$$

or $$V_1 = \frac{w}{Mp}RT$$

$$= \frac{0.184\times0.0821\times(273+17)}{2p} = \frac{2.1904}{p}$$

Volume occupied by 3.7 g of gas at 25°C and at same pressure.

$$V_2 = \frac{w}{Mp}RT = \frac{3.7\times0.0821\times298}{Mp} = \frac{90.523}{Mp}$$

Now $V = V_2 = \frac{2.1904}{p} = \frac{90.523}{Mp}$

or $M = \frac{90.523}{2.1904} = \mathbf{41.3}$

25. At equilibrium, 20% i.e., 0.2 mole is dissociated

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial conc.	1		0
At equ.	(1 – 0.2)		2 × 0.2
	= 0.8		= 0.4

Molar mass of mixture = $\frac{0.8\times92 + 0.4\times46}{0.8+0.4} = 76.66$

$$pV = \frac{w}{M}RT$$

or $$d = \frac{w}{V} = \frac{p\times M}{RT} = \frac{1\times76.66}{0.082\times300} = \mathbf{3.11\ gL^{-1}.}$$

26. Partial pressure of N_2 in 2 L flask, $p_{N_2} = \frac{p_1V_1}{V_2}$

$$= \frac{500\times0.936}{2000} = 0.234 \text{ bar}$$

Partial pressure of O_2 in 2 L flask, $p_{O_2} = \frac{p_1V_1}{V_2}$

$$= \frac{1000\times0.80}{2000} = 0.40 \text{ bar}$$

Total pressure = $p_{N_2} + p_{O_2}$ = 0.234 + 0.40 = **0.634 bar.**

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27.

$p_1 = p_{total}$ – aq. tension $\quad p_2 = 1$ bar

$= 0.948 - 0.0318 = 0.9162$ bar

$V_1 = 400\ mL \quad V_2 = ?$

$T_1 = 273 + 25 = 298$ K $\quad T_2 = 273$ K

Now $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$ or $V_2 = \frac{p_1V_1T_2}{p_2T_1}$

$\therefore \quad V_2 = \frac{0.9162 \times 400 \times 273}{1 \times 298} = \mathbf{335.7\ mL.}$

28. Partial pressure of gases,

$p(SO_2) = \frac{nRT}{V} = \frac{0.25 \times 8.314 \times 300}{2.5 \times 10^{-3}} = 2.49 \times 10^5$ Pa

$p(N_2) = \frac{nRT}{V} = \frac{0.25 \times 8.314 \times 300}{2.5 \times 10^{-3}} = 2.49 \times 10^5$ Pa

$P_{total} = 2.49 \times 10^5 + 2.49 \times 10^5 = \mathbf{4.98 \times 10^5\ Pa.}$

29. Molar mass of SO_3 $= 32 + 3 \times 16 = 80$,

Molar mass of He $= 4.0$

Moles of $SO_3 = \frac{19.5}{80} = 0.244$

Moles of He $= \frac{1.0}{4.0} = 0.25$

Partial pressure of SO_3, $p_{(SO_3)} = \frac{nRT}{V}$

$= \frac{0.25 \times 0.0821 \times 293}{5.0} = 1.17$ atm

Partial pressure of He, $p_{(He)} = \frac{nRT}{V}$

$= \frac{0.25 \times 0.0821 \times 293}{5.0} = 1.20$ atm

Total pressure $= p_{(SO_3)} + p_{(He)} = 1.17 + 1.20$

$= \mathbf{2.37\ atm.}$

30. $p_{(N_2)} = \frac{nRT}{V} = \frac{1.0 \times 0.08314 \times 298}{10}$

$= 2.48$ bar

$p_{(H_2)} = \frac{3.0 \times 0.08314 \times 298}{10} = 7.43$ bar

Total pressure $= p(N_2) + p(H_2) = 2.48 + 7.43$

$= \mathbf{9.91\ bar.}$

31. Moles of $CH_4 = \frac{3.2}{16} = 0.2$

$p_{(CH_4)} = \frac{nRT}{V} = \frac{0.2 \times 8.314 \times 300}{9 \times 10^{-3}}$

$= 5.54 \times 10^4$ Pa

Moles of $CO_2 = \frac{4.4}{44} = 0.1$

$p_{(CO_2)} = \frac{0.1 \times 8.314 \times 300}{9 \times 10^{-3}} = 2.77 \times 10^4$ Pa

Total pressure $= 5.54 \times 10^4$ Pa $+ 2.77 \times 10^4$ Pa

$= \mathbf{8.31 \times 10^4\ Pa}$

32. Let us first calculate mol fraction of each component.

Moles of $N_2 = \frac{75.5}{28} = 2.696$,

Moles of $O_2 = \frac{23.2}{32} = 0.725$

Moles of Ar $= \frac{1.3}{40} = 0.0325$

Total moles $= 2.696 + 0.725 + 0.0325 = 3.4535$

Mole fraction of N_2, $x_{N_2} = \frac{2.696}{3.4535} = 0.781$,

Mole fraction of O_2, $x_{O_2} = \frac{0.725}{3.4535} = 0.210$

Mole fraction of Ar, $x_{Ar} = \frac{0.0325}{3.4535} = 0.0094$

$p_{(N_2)} = x_{N_2} \times p = 0.781 \times 1 = \mathbf{0.781\ bar}$

$p_{(O_2)} = x_{O_2} \times p = 0.210 \times 1 = \mathbf{0.210\ bar}$

$p_{(Ar)} = x_{Ar} \times p = 0.009 \times 1 = \mathbf{0.0094\ bar.}$

33. Partial pressure of N_2, $p_{(N_2)} = \frac{2.0}{28} \times \frac{0.0821 \times 300}{1.0}$

$= 1.76$ atm

Partial pressure of H_2, $p_{(H_2)} = \frac{0.4}{2} \times \frac{0.0821 \times 300}{1.0}$

$= 4.93$ atm

Partial pressure of O_2, $p(O_2) = \frac{9.0}{32} \times \frac{0.0821 \times 300}{1.0}$

$= 6.93$ atm

Total pressure $= p_{N_2} + p_{(H_2)} + p_{(O_2)}$

$= 1.76 + 4.93 + 6.93$

$= \mathbf{13.62\ atm.}$

34. Let aqueous tension at 15°C $= x$ mm Hg

The pressure of dry gas $= (745 - x)$ mm Hg

Now, $p_1 = (745 - x)$ mm Hg $\quad p_2 = 760$ mm Hg

$V_1 = 200\ cm^3 \quad V_2 = 182.6\ cm^3$

$T_1 = 273 + 15 = 288$ K $\quad T_2 = 273$ K

Applying $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$

$\frac{(745 - x) \times 200}{288} = \frac{760 \times 182.6}{273}$

$(745 - x) = \frac{760 \times 182.6 \times 288}{273 \times 200} = 732$

$x = 745 - 732 = \mathbf{13\ mm\ Hg.}$

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O 35. Mass of $H_2 = 20\ g$, Mass of $O_2 = 80\ g$

$$\text{Moles of } H_2 = \frac{20}{2} = 10 \text{ mol, Moles of } O_2 = \frac{80}{32} = 2.5 \text{ mol}$$

$$\text{Mole fraction of } H_2 = \frac{10}{10+2.5} = 0.8$$

Partial pressure $= 0.8 \times p = 0.8 \times 1$ bar $=$ **0.8 bar**

O 36. $$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

M_1 = Mol. wt. of $^{235}UF_6 = 235 + 6 \times 19 = 349$

M_2 = Mol. wt. of $^{238}UF_6 = 238 + 6 \times 19 = 352$

$$\frac{r(^{235}UF_6)}{r(^{238}UF_6)} = \sqrt{\frac{352}{349}} = 1.004$$

$\therefore$ $r(^{235}UF_6) : r(^{238}UF_6) = 1.004 : 1.$

O 37. According to Graham's law of diffusion,

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

For gas X,

$$r_1(X) = \frac{35}{t} \qquad M_1 = ?$$

For Cl_2 gas,

$$r_2 = \frac{29}{t}, \qquad M_2 = 71$$

$$\frac{35/t}{29/t} = \sqrt{\frac{71}{M_1}}$$

or $$\left(\frac{35}{29}\right)^2 = \frac{71}{M_1}$$

or $$M_1 = \frac{71 \times 29 \times 29}{35 \times 35} = \mathbf{48.75.}$$

O 38. $$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Let time taken by H_2 to effuse $= x$ sec

Time taken by gas G to effuse $= 4x$

$$\frac{t_G}{t_{H_2}} = \frac{4x}{x} = \sqrt{\frac{M(G)}{M(H_2)}} = \sqrt{\frac{M(G)}{2}}$$

$$\frac{4}{1} = \sqrt{\frac{M(G)}{2}} \text{ or } M(G) = 16 \times 2 = \mathbf{32.}$$

O 39. $$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}} \quad \text{or} \quad \frac{t_B}{t_A} = \sqrt{\frac{M_B}{M_A}}$$

$t_A = 20$ sec, $t_B = 10$ sec, $M_A = 80$, $M_B = ?$

$$\frac{10}{20} = \sqrt{\frac{M_B}{80}}$$

$$M_B = \frac{80}{4} = \mathbf{20\ g\ mol^{-1}.}$$

O 40. Rate of diffusion of a gas is inversely proportional to its molar of mass. Since molar mass of NH_3 is less than HCl, NH_3 will diffuse faster.

Now $$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{\frac{M(HCl)}{M(NH_3)}}$$

$$= \sqrt{\frac{36.5}{17}}$$

$$= \sqrt{2.174} = \mathbf{1.46}$$

$\therefore$ NH_3 will diffuse 1.46 times faster than HCl.

O 41. $$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Rate of diffusion of hydrocarbon, $r_1 = \frac{180}{15}$

Rate of diffusion of sulphur dioxide, $r_2 = \frac{120}{20}$

$$\frac{180/15}{120/20} = \sqrt{\frac{64}{M\text{ (hydrocarbon)}}}$$

or $$2 = \sqrt{\frac{64}{M\text{ (hydrocarbon)}}}$$

or $$M\text{ (hydrocarbon)} = \frac{64}{4} = 16$$

Molecular formula will be **CH_4 (Methane).**

O 42. $$\frac{t_{mix}}{t_{O_2}} = \sqrt{\frac{M_{mix}}{M_{O_2}}}$$

$$\frac{245}{220} = \sqrt{\frac{M_{mix}}{32}}$$

$$M_{mix} = 39.68$$

As the mixture contains 20 mole% of X, then, if n is the total number of moles,

$$\text{moles of } O_2 = \frac{n \times 80}{100} = 0.80n$$

$$\text{moles of gas X} = \frac{n \times 20}{100} = 0.20n$$

$$M_{mix} = \frac{32 \times 0.8n + M_X \times 0.2n}{n}$$

$$39.68 = 25.6 + 0.2\ M_X$$

$$0.2\ M_X = 39.68 - 25.6 = 14.08$$

$\therefore$ $$M_X = \frac{14.8}{0.2} = \mathbf{70.4}$$

O 43. Comparing rates of diffusion of gas B and Gas C .

$$\frac{r_B}{r_C} = \sqrt{\frac{M_C}{M_B}}$$

$M_C = 128$, $= \frac{r_B}{r_C} = 2$, MB = ?

$$2 = \sqrt{\frac{128}{M_B}}$$

or $$4 = \frac{128}{M_B}$$

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$$\therefore \quad M_B = \frac{128}{4} = 32$$

Now, comparing rates of diffusion of gas B and A

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$$

$$\frac{r_A}{r_B} = 4, M_B = 32, M_A = ?$$

$$4 = \sqrt{\frac{32}{M_A}}$$

or $$16 = \frac{32}{M_A}$$

$$\therefore \quad M_A = \frac{32}{16} = \mathbf{2\ g\ mol^{-1}.}$$

44. $$E_k = \frac{3}{2} nRT$$

$$= \frac{3}{2} \times 2 \times 8.314 \times 300 = 7482.6\ J = \mathbf{7.48\ kJ.}$$

45. Average kinetic energy of a gas molecule

$$= \frac{3}{2} k_b.T = \frac{3}{2} \frac{RT}{N_A}$$

$$= \frac{3}{2} \times \frac{8.314 \times 300}{6.022 \times 10^{23}} = \mathbf{6.21 \times 10^{-21}\ J.}$$

46. Kinetic energy, $E_k = \frac{3}{2} nRT$

$$\therefore \quad 2182\ J = \frac{3}{2} \times 0.5 \times 8.314 \times T$$

$$T = \frac{2182 \times 2}{3 \times 0.5 \times 8.314} = 349.9\ K$$

or $$\boldsymbol{t = 76.9°C}$$

47. $$u_{r.m.s} = \sqrt{\frac{3RT}{M}}$$

For methane, $M = 16, T = 27 + 273 = 300\ K$

$$u_{r.m.s}(CH_4) = \sqrt{\frac{3R \times 300}{16}}$$

For SO_2, $M = 64, T = ?$

Now $$u_{r.m.s}(SO_2) = \sqrt{\frac{3R \times T}{64}}$$

$$\sqrt{\frac{300}{16}} = \sqrt{\frac{T}{64}}$$

$$\therefore \quad T = \frac{300 \times 64}{16} = 1200$$

$$t = 1200 - 273 = \mathbf{927°C}$$

48. Root mean square velocity of methane at temperature T

$$u_{r.m.s}(\text{at } T) = \sqrt{\frac{3RT}{M}}$$

Root mean square velocity of methane at N.T.P.

$$u_{r.m.s}(\text{N.T.P.}) = \sqrt{\frac{3RT'}{M}} = \sqrt{\frac{3R \times 273}{M}}$$

Now $$u_{r.m.s}(T) = 2\, u_{r.m.s}(\text{N.T.P.})$$

$$\sqrt{\frac{3RT}{M}} = 2\sqrt{\frac{3R \times 273}{M}}$$

$$\therefore \quad T = 4 \times (273) = 1092\ K$$

or $$t = 1092 - 273 = \mathbf{819°C}$$

49. $$u_{r.m.s} = \sqrt{\frac{3pV_m}{M}}$$

$p = 1\ atm = 76\ cm = 76 \times 13.6 \times 981\ dynes\ cm^{-2}$

$V = 22400\ cm^3, M = 40$

$$u_{r.m.s} = \sqrt{\frac{3 \times 76 \times 13.6 \times 981 \times 22400}{40}}$$

$$= \mathbf{4.127 \times 10^4\ cm\ sec^{-1}.}$$

50. According to van der Waals gas equation,

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

or $$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

Now $V = 5\ L, T = 273 + 27 = 300\ K, n = 2\ mol,$
$R = 0.082\ L\ bar\ mol^{-1}\ K^{-1}$

$$\therefore \quad p = \frac{2 \times 0.082 \times 300}{5 - 2 \times 0.0371} - \frac{4.17 \times 4}{25}$$

$$= 9.99 - 0.67 = \mathbf{9.32\ bar.}$$

51. $n = 3\ mol, p = 150\ atm, V = 10\ L,$
$R = 0.082\ L\ atm\ mol^{-1}\ K^{-1}$

According to ideal gas equation,

$$pV = nRT \quad \text{or} \quad T = \frac{pV}{nR}$$

$$T = \frac{15 \times 10}{3 \times 0.082} = \mathbf{609.8\ K}$$

Using van der Waals equation,

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$T = \frac{\left(p + \frac{an^2}{V^2}\right)(V - nb)}{nR}$$

or $$T = \frac{\left(15 + \frac{6.7 \times (3)^2}{10^2}\right)(10 - 3 \times 0.0564)}{3 \times 0.082}$$

$$= \frac{15.603 \times 9.8308}{0.246} = \mathbf{623.54}\ .$$

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Chapter Summary

Key Terms & Laws

- **Ideal gas.** A gas which obeys the gas laws and the gas equation ($pV = nRT$) strictly at all temperatures and pressures.
- **Real gas.** A gas which does not obey ideal gas equation and other gas laws at all temperatures and pressures.
- Van der Waals' equation : $\left(p + \frac{an^2}{V}\right)(V - nb) = nRT$.
- **Critical temperature.** The temperature above which a gas cannot be liquefied however high the pressure may be applied.
- **Critical pressure.** The minimum pressure required to liquefy the gas at critical temperature.
- **Critical volume** is the volume occupied by one mole of the gas at critical temperature and pressure.
- **Vapour pressure.** The pressure exerted by the vapours of the liquid in equilibrium with the liquid at a particular temperature.
- **Boiling point.** The temperature at which vapour pressure of the liquid becomes equal to the atmospheric pressure.
- **Surface tension.** The force per unit length acting perpendicular to the tangential line on the surface.
- **Viscosity.** The internal resistance to flow in liquids which one layer offers to another layer trying to pass over it.

QUICK CHAPTER ROUND UP

GASEOUS STATE

Weakest intermolecular interactions but highest thermal energy

Gas Laws

- **Boyle's law**
$$p_1V_1 = p_2V_2 \text{ (constant T, } n)$$
- **Charles' law**
$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{(constant } p, n)$$
- **Avogadro's law**
$$V \propto n \text{ } (p, \text{T constant})$$
or $$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$
- **Ideal gas equation**
$$pV = nRT$$
- **Density and molar mass relation**
$$M = \frac{dRT}{p}$$
- **Dalton's law**
$$p = p_1 + p_2 + p_3 + ...$$
$$p_i = x_i \times p$$
- **Graham's law**
$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

- **Kinetic gas equation**
$$pV = \frac{1}{3}mN\bar{\mu}^2$$
- **Kinetic energy for *n* moles of gas**
$$E_k = \frac{3}{2}nRT$$
- **Average kinetic energy per molecule**
$$E_k = \frac{3}{2}k_bT$$
(k_b = Boltzmann constant)

- **Most probable speed,** $u_{mp} = \sqrt{\frac{2RT}{M}}$
- **Average speed,** $u_{av} = \sqrt{\frac{8RT}{\pi M}}$
- **Root mean square speed,** $u_{r.m.s.} = \sqrt{\frac{3RT}{M}}$
- **Average speed** (u_{av}) = 0.9213 × Root mean square speed ($u_{r.m.s.}$)
- **Most probable speed** (u_{mp}) = 0.816 × Root mean square speed ($u_{r.m.s.}$)

or $u_{mp} : u_{av} : u_{r.m.s.} = 1 : 1.128 : 1.224$

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The hypothetical temperature at which all gases are supposed to occupy zero volume is called **absolute zero temperature**. (It is numerically equal to –273.15°C or 0 K).

Van der Waals equation

$$\left(p + \frac{an^2}{V}\right)(V - nb) = nRT$$

Units: $a \Rightarrow$ atm L^2 mol^{-2}

$b \Rightarrow$ L mol^{-1}

- **at low pressure**
  $$pV = RT - a/V$$
- **at high pressure**
  $$pV = RT + pb$$
- **at high temperature and low pressure**
  $pV = RT$ (ideal gas equation)

Surface tension

- decreases with rise in temperature
- **Units** : Nm^{-1} or dyne cm^{-1}

The root mean square speed is commonly used and can be calculated from the following relations :

$$u_{r.m.s.} = \sqrt{\frac{3RT}{M}} \text{ or } \sqrt{\frac{3pV}{M}} \text{ or } \sqrt{\frac{3p}{\rho}}$$

Compressibility factor

$$Z = \frac{pV}{nRT}$$

(*i*) If Z < 1, it is called **negative deviation**. It means that *the gas is more compressible than expected from ideal behaviour.*

(*ii*) If Z > 1, it is called **positive deviation.** It means that *the gas is less compressible than expected from ideal behaviour.*

(*iii*) If Z = 1, it is **ideal gas behaviour**.

$$T_c = \frac{8a}{27Rb}$$

$$p_c = \frac{a}{27b^2}$$

$$V_c = 3b$$

Viscosity

- decreases with rise in temperature
- **Units** : Pa.s or Nm^{-2} s

NCERT FILE Solved

NCERT Textbook Exercises

Q. 1. What will be the minimum pressure required to compress 500 dm^3 of air at 1 bar to 200 dm^3 at 30°C.

Ans. $p_1V_1 = p_2V_2$ (at constant T)

$$p_2 = \frac{p_1V_1}{V_2}$$

$$= \frac{(1\,\text{bar}) \times (500\,\text{dm}^3)}{(200\,\text{dm}^3)}$$

$$= 2.5 \text{ bar}$$

Q. 2. A vessel of 120 mL capacity contains a certain amount of gas at 35°C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35°C. What would be its pressure?

Ans. *Refer Solved Example 2 (Page 12).*

Q. 3. Using the equation of state $pV = nRT$; show that at a given temperature density of a gas is proportional to gas pressure p.

Ans. $pV = nRT$

or $$p = \frac{nRT}{V}$$

Now, number of moles $(n) = \frac{\text{Mass of substance}\,(m)}{\text{Molar mass}\,(M)}$

$$p = \frac{mRT}{MV}$$

But $\frac{m}{V}$ = density, d so that

$$p = \frac{dRT}{M}$$

or $$d = \frac{pM}{RT}$$

or $d \propto p$ (for a given gas at constant T)

Thus, at a given temperature density of a gas is proportional to gas pressure.

Q. 4. At 0°C, the density of a certain oxide of a gas at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide?

Ans. Density, $d = \frac{Mp}{RT}$

At the same temperature and for the same density.

$$M_1p_1 = M_2p_2$$

(Gaseous oxide) (N_2)

$$M_1 \times (2 \text{ bar}) = 28 \times (5 \text{ bar})$$

$$M_1 = \frac{28 \times 5}{2} = 70 \text{ u}$$

Q. 5. Pressure of 1 g of an ideal gas A at 27°C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature the pressure becomes 3 bar. Find a relationship between their molecular masses.

Ans. Let the molecular masses of A and B are M_A and M_B respectively.

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Moles of gas A = $\frac{1}{M_A}$

Moles of gas B = $\frac{2}{M_B}$

p_A = 2 bar

$p_A + p_B$ = 3 bar so that $p_B = 3 - 2 = 1$ bar

Applying gas equation,

$p_A V = n_A RT$ ...(*i*)

$p_B V = n_B RT$ ...(*ii*)

Dividing eqn. (*i*) by eqn. (*ii*)

$$\frac{p_A}{p_B} = \frac{n_A}{n_B} = \frac{1/M_A}{2/M_B} = \frac{M_B}{2M_A}$$

or $$\frac{M_B}{M_A} = 2\frac{p_A}{p_B} = 2 \times \frac{2}{1} = 4$$

$\therefore$ $M_B = \mathbf{4\,M_A}$.

Q. 6. The drain cleaner, Drainex contains small bits of aluminium which react with caustic soda to produce dihydrogen. What volume of dihydrogen at 20°C and one bar will be released when 0.15g of aluminium reacts?

Ans. *Refer Solved Example 23 (Page 21).*

Q. 7. What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in a 9 dm^3 flask at 27°C ?

Ans. Moles of $CH_4 = \frac{3.2}{16} = 0.2$

$$p_{(CH_4)} = \frac{nRT}{V}$$

$$= \frac{0.2\ \text{mol} \times (8.314\ \text{Pa m}^3\text{K}^{-1}\text{mol}^{-1}) \times 300\text{K}}{9 \times 10^{-3}\ \text{m}^3}$$

$$= 5.54 \times 10^4\ \text{Pa}$$

Moles of $CO_2 = \frac{4.4}{44} = 0.1$

$$p_{(CO_2)} = \frac{0.1\text{mol} \times (8.314\ \text{Pa m}^3\text{K}^{-1}\text{mol}^{-1}) \times 300\text{K}}{9 \times 10^{-3}\ \text{m}^3}$$

$$= 2.77 \times 10^4\ \text{Pa}$$

Total pressure = 5.54×10^4 Pa + 2.77×10^4 Pa

= **8.31×10^4 Pa**

Q. 8. What will be the pressure of the gaseous mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a 1L vessel at 27°C?

Ans. *Refer Solved Example 29 (Page 25).*

Q. 9. Density of a gas is found to be 5.49 g/dm^3 at 27°C at 2 bar pressure. What will be its density at STP?

Ans. *Refer Solved Example 26 (Page 22).*

Q. 10. 34.05 mL of phosphorus vapour weighs 0.0625 g at 546°C and 1 bar pressure. What is the molar mass of phosphorus?

Ans. Molecular mass of phosphorus, $M = \frac{wRT}{pV}$

w = 0.0625 g,

V = 34.05 mL = 34.05×10^{-3} L,

p = 1.0 bar

T = 273 + 546 = 819 K,

R = 0.08314 L bar K^{-1} mol^{-1}

$$M = \frac{0.0625\ \text{g} \times (0.08314\ \text{bar L K}^{-1}\text{mol}^{-1}) \times 819\ \text{K}}{1 \times 34.05 \times 10^{-3}\ \text{L}}$$

$$= 124.98\ \text{g mol}^{-1}$$

Q. 11. A student forgot to add the reaction mixture to the round bottomed flask at 27°C but instead he/she placed the flask on the flame. After a lapse of time, he realized his mistake and using a pyrometer he found the temperature of the flask was 477°C. What fraction of air would have been expelled out?

Ans. $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

T_1 = 273 + 27 = 300 K

T_2 = 273 + 477 = 750 K

$\frac{V_1}{V_2} = \frac{300}{750} = \frac{2}{5}$

Fraction of gas expelled = $1 - \frac{2}{5} = \frac{3}{5}$

Q. 12. Calculate the temperature of 4.0 mol of a gas occupying 5 dm^3 at 3.32 bar. (R = 0.083 bar dm^3 K^{-1} mol^{-1})

Ans. *Refer Solved Example 20 (Page 20).*

Q. 13. Calculate the total number of electrons present in 1.4 g of dinitrogen gas.

Ans. Moles of dinitrogen = $\frac{1.4}{28} = 0.05$

No. of molecules of dinitrogen = $0.05 \times 6.02 \times 10^{23}$

= 3.011×10^{22}

No. of electrons in one molecule of N_2 = 14

$\therefore$ No. of electrons in 1.4 g of N_2 = $3.011 \times 10^{22} \times 14$

= 4.2154×10^{23}

Q. 14. How much time would it take to distribute one Avogadro number of wheat grains, if 10^{10} grains are distributed each second?

Ans. Avogadro number = 6.022×10^{23}

10^{10} grains are distributed in = 1 sec.

6.022×10^{23} grains would be distribtued in

$$= \frac{6.022 \times 10^{23}}{10^{10}}\ \text{sec}$$

$$= \frac{6.022 \times 10^{23}}{10^{10} \times 3600 \times 24 \times 365}$$

= **1.9096×10^6 years.**

Q. 15. Calculate the total pressure in a mixture of 8 g of dioxygen and 4 g of dihydrogen confined in a vessel of 1 dm^3 at 27°C. R = 0.083 bar dm^3 K^{-1} mol^{-1}.

Ans. *Refer Solved Example 30 (Page 25).*

Q. 16. Pay load is defined as the difference between the mass of displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10m, mass 100 kg is filled with helium at 1.66 bar at 27°C. (Density of air = 1.2 kg m^{-3} and R = 0.083 bar dm^3 K^{-1} mol^{-1}).

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Ans. *Refer Solved Example 21 (Page 21).*

Q. 17. Calculate the volume occupied by 8.8 g of CO_2 at 31.1°C and 1 bar pressure. R = 0.083 bar LK^{-1} mol^{-1}.

Ans. *Refer Solved Example 18 (Page 20).*

Q. 18. 2.9 g of gas at 95°C occupied the same volume as 0.184 g of dihydrogen at 17°C, at the same pressure. What is the molar mass of the gas?

Ans. *Refer Solved Example 22 (Page 21).*

Q. 19. A mixture of dihydrogen and dioxygen at one bar pressure contains 20% by weight of dihydrogen. Calculate the partial pressure of dihydrogen.

Ans. Mass of H_2 = 20 g,
Mass of O_2 = 80 g

$$\text{Moles of } H_2 = \frac{20}{2} = 10 \text{ mol},$$

$$\text{Moles of } O_2 = \frac{80}{32} = 2.5 \text{ mol}$$

$$\text{Mole fraction of } H_2 = \frac{10}{10 + 2.5} = 0.8$$

Partial pressure = $0.8 \times p = 0.8 \times 1$ bar = **0.8 bar**

Q. 20. What would be the SI unit for the quantity $pV^2 T^2/n$?

Ans.
$$\frac{pV^2T^2}{n} = \frac{(Nm^{-2})\,(m^3)^2(K)^2}{mol}$$
$$= Nm^4 K^2 mol^{-1}$$

Q. 21. In terms of Charles' law explain why –273°C is the lowest possible temperature.

Ans. At –273°C, volume of the gas becomes equal to zero i.e., the gas ceases to exist.

Q. 22. Critical temperature of carbon dioxide and water are 31.1°C and –81.9°C respectively. Which of these has stronger intermolecular forces and why ?

Ans. Higher the critical temperature, more easily the gas can be liquefied i.e., greater are the intermolecular forces of attraction. Therefore, CO_2 has stronger intermolecular forces than H_2O.

Q. 23. What is the significance of the van der Waals constants 'a' and 'b' ?

Ans. '*a*' is a measure of magnitude of intermolecular forces of attraction.
'*b*' is a measure of the effective size of the molecules.

NCERT Exemplar Problems

Subjective Questions

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 94.*

Short Answer Questions *carrying 2 or 3 marks*

Q. 1. If 1 gram of each of the following gases are taken at STP, which of the gases will occupy : (*a*) greatest volume and (*b*) smallest volume ?
CO, H_2O, CH_4, NO

Ans. Molar volume of a gas is volume occupied by 1 mole of gas at STP (273.15 K and 1 bar pressure) and is equal to 22700 mL

28 g of CO occupy volume = 22700 mL

$$\therefore \text{ 1g of CO occupies volume} = \frac{22700}{28} \text{ mL at STP}$$

Similarly,

$$\text{1g of } H_2O \text{ occupies volume} = \frac{22700}{18} \text{ mL at STP}$$

$$\text{1g of } CH_4 \text{ occupies volume} = \frac{22700}{16} \text{ mL at STP}$$

$$\text{1g of NO occupies volume} = \frac{22700}{30} \text{ mL at STP}$$

(*a*) CH_4 occupies greatest volume
(*b*) NO occupies smallest volume.

Q. 2. Physical properties of ice, water and steam are very different. What is the chemical composition of water in all the three states.

Ans. Chemical composition is same in all the phases *i.e.*, H_2O.

Q. 3. The behaviour of matter in different states is governed by various physical laws. According to you what are the factors that determine the state of matter ?

Ans. The factors which determine the state of matter are pressure, temperature, mass and volume.

Q. 4. Use the information and data given below to answer the questions (a) to (c)

- **Stronger intermolecular forces result in higher boiling point.**
- **Strength of London forces increases with the number of electrons in the molecule.**
- **Boiling point of HF, HCl, HBr and HI are 293 K, 189 K, 206 K and 238 K respectively.**

(*a*) Which type of intermolecular forces are present in the molecules HF, HCl, HBr and HI?

(*b*) Looking at the trend of boiling points of HCl, HBr and HI, explain out of dipole-dipole interaction and London interaction, which one is predominant here.

(*c*) Why is boiling point of hydrogen fluoride highest while that of hydrogen chloride lowest ?

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Ans. (*a*) In HCl, HBr and HI, dipole-dipole and London forces are present because the molecules possess permanent dipole. In HF dipole-dipole, London forces and hydrogen bonding are present.

(*b*) Electronegativity of Cl, Br and I decreases in the order : Cl > Br > I

Therefore polar character and hence dipole-dipole interactions should decrease from HCl to HI. But boiling point increases in the order : HCl < HBr < HI. This means that London forces are predominant. This is because London forces increase as the number of electrons in a molecule increases. In this case number of electrons increases from HCl to HI.

(*c*) Due to high electronegativity of F, HF is most polar and hydrogen bonding is also present in it. Hence, HF has highest boiling point.

Q.5. What will be the molar volume of nitrogen and argon at 273.15 K and 1 atm ?

Ans. 22.4 L because every gas at 1 atm pressure and 273.15 K has molar volume = 22.4 L.

Q.6. A gas that follows Boyle's law, Charle's law and Avogadro's law is called an ideal gas. Under what conditions a real gas would behave ideally?

Ans. A real gas behaves as an ideal gas when the pressure is low and temperature is high.

Q.7. Two different gases 'A' and 'B' are filled in separate containers of equal capacity under the same conditions of temperature and pressure. On increasing the pressure slightly the gas 'A' liquefies but gas B does not liquify even on applying high pressure until it is cooled. Explain this phenomenon.

Ans. Gas 'A' is at critical temperature and therefore liquefies. Gas 'B' is at a temperature higher than critical temperature and therefore, does not liquify even on applying high pressure.

Q.8. Value of universal gas constant (R) is same for all gases. What is its physical significance ?

Ans. From the gas equation,

$$pV = nRT, \quad R = \frac{pV}{nT}$$

If p is measured in Pascal, V in m^3, n in mol and T in Kelvin, then units of R are

$$R = \frac{Pa\ m^3}{mol\ K} = Pa\ m^3\ K^{-1}\ mol^{-1}$$

or $J\ mol^{-1}\ K^{-1}$.

Since Joule is a unit of work then R represents work done per mole per Kelvin.

Q.9. One of the assumptions of kinetic theory of gases states that "there is no force of attraction between the molecules of a gas." How far is this statement correct ? Is it possible to liquefy an ideal gas ? Explain.

Ans. The given statement is correct for ideal gases. In the absence of intermolecular forces of attraction, it will not be possible to liquefy an ideal gas.

Q.10. The magnitude of surface tension of liquid depends on the attractive forces between the molecules. Arrange the following in increasing order of surface tension :

water, alcohol (C_2H_5OH) and hexane [$CH_3(CH_2)_4(CH_3)$].

Ans. Hexane < alcohol < water.

Q.11. Pressure exerted by saturated water vapour is called aqueous tension. What correction term will you apply to the total pressure to obtain pressure of dry gas ?

Ans. p(dry gas)= p(moist gas)

or = total pressure – aqueous tension

Q.12. Name the energy which arises due to motion of atoms or molecules in a body. How is this energy affected when the temperature is increased?

Ans. Thermal energy. It is a measure of average kinetic energy of particles. It increases with increase of temperature.

Q.13. Name two intermolecular forces that exist between HF molecules in liquid state.

Ans. (*i*) Dipole-dipole interactions

(*ii*) Hydrogen bonding

Q.14. One of the assumptions of kinetic theory of gases is that there is no force of attraction between the molecules of a gas.

State and explain the evidence that shows that the assumption is not applicable for real gases.

Ans. Real gases can be liquefied on cooling and compressing showing that forces of attraction exist between the molecules.

Q.15. Compressibility factor, Z, of a gas is given as

$$Z = \frac{pV}{nRT}$$

(*i*) What is the value of Z for an ideal gas ?

(*ii*) For real gas what will be the effect on value of Z above Boyle's temperature ?

Ans. (*i*) For an ideal gas Z = 1

(*ii*) For a real gas above Boyle's temperature, Z > 1.

Q.16. The critical temperature (T_c) and critical pressure (p_c) of CO_2 are 30.98°C and 73 atm respectively. Can CO_2 (g) be liquefied at 32°C and 80 atm pressure ?

Ans. CO_2 gas cannot be liquefied at 32°C by applying a pressure of 80 atm. This is because the temperature is higher than critical temperature of CO_2.

Q.17. The van der Waals equation for real gases is :

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

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where '*a*' and '*b*' are van der Waals constants, '*nb*' is approximately equal to the total volume of molecules of a gas. '*a*' is the measure of magnitude of intermolecular attraction.

(*i*) Arrange the following gases in the increasing order of '*b*'. Give reason.

O_2, CO_2, H_2, He.

(*ii*) Arrange the following gases in the decreasing order of magnitude of '*a*'. Give reason.

CH_4, O_2, H_2

Ans. (*i*) $H_2 < He < O_2 < CO_2$. This is because of increase in size.

(*ii*) $CH_4 > O_2 > H_2$. This is because intermolecular forces are the highest in CH_4 and the lowest in H_2 because intermolecular forces increase with increase in number of electrons in a molecule.

Q.18. The relation between pressure exerted by an ideal gas (p_{ideal}) and observed pressure (p_{real}) is given by the equation

$$p_{ideal} = p_{real} + \frac{an^2}{V^2}$$

If pressure is taken in Nm^{-2}, number of moles in mol and volume in m^3, calculate the unit of '*a*'.

What will be the unit of '*a*' when pressure is in atmosphere and volume in dm^3?

Ans. $p_{ideal} = p_{real} + \frac{an^2}{V^2}$

If pressure is in Nm^{-2}

$$\frac{an^2}{V^2} = p_{ideal} - p_{real}$$

$$\frac{a\,mol^2}{m^6} = Nm^{-2} - Nm^{-2} = Nm^{-2}$$

$$\text{or } a = \frac{Nm^{-2} \times m^6}{mol^2} = \mathbf{Nm^4\ mol^{-2}}$$

If pressure is in atm

$$\frac{a\,mol^2}{dm^6} = \text{atm or } a = \text{atm } dm^6\ mol^{-2}$$

Q.19. Name two phenomena that can be explained on the basis of surface tension.

Ans. (*i*) Spherical shape of small liquid drops.

(*ii*) Rise or fall of the liquid in a capillary *i.e.*, capillary action.

Q.20. Viscosity of a liquid arises due to strong intermolecular forces existing between the molecules. Stronger the intermolecular forces, greater is the viscosity. Name the intermolecular forces existing in the following liquids and arrange them in the increasing order of their viscosities. Also give reason for the assigned order in one line.

Water, hexane ($CH_3\,CH_2\,CH_2\,CH_2\,CH_2\,CH_3$), glycerine ($CH_2OH\,CH(OH)\,CH_2OH$).

Ans. The increasing order of viscosity is

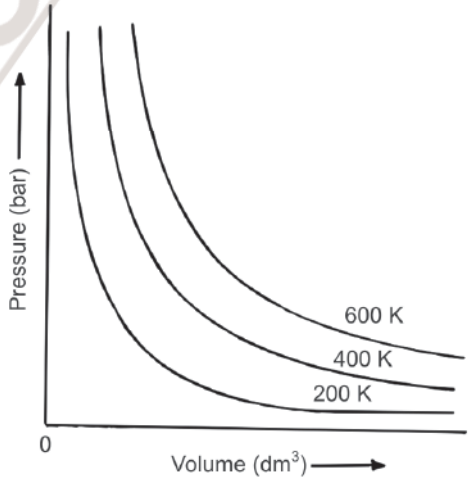
Hexane < Water < Glycerine

In hexane, there are only London forces, whereas in water and glycerine there are hydrogen bonding which is strong in case of glycerine (because of presence of three – OH groups) than that in water.

Q.21. Explain the effect of increasing the temperature of a liquid, on intermolecular forces operating between its particles, what will happen to the viscosity of a liquid if its temperature is increased ?

Ans. The viscosity of a liquid decreases with the increase in temperature because the kinetic energy of the molecules can overcome intermolecular forces of attraction. Therefore, the liquid can flow more easily.

Q.22. The variation of pressure with volume of the gas at different temperatures can be graphically represented as shown in following figure.



On the basis of this graph answer the following questions.

(*i*) How will the volume of a gas change if its pressure is increased at constant temperature?

(*ii*) At a constant pressure, how will the volume of a gas change if the temperature is increased from 200K to 400K?

Ans. (*i*) The volume of a gas will decrease if the pressure on the gas is increased keeping the temperature constant.

(*ii*) On increasing temperature, the volume of a gas will increase if the pressure is kept constant.

Q.23. Pressure versus volume graph for a real gas and an ideal gas are shown in the figure given below. Answer the following questions on the basis of this graph.

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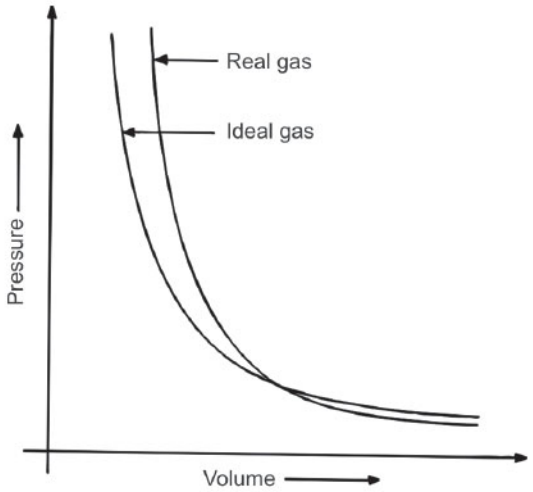


(*i*) Interpret the behaviour of real gas with respect to ideal gas at low pressure.

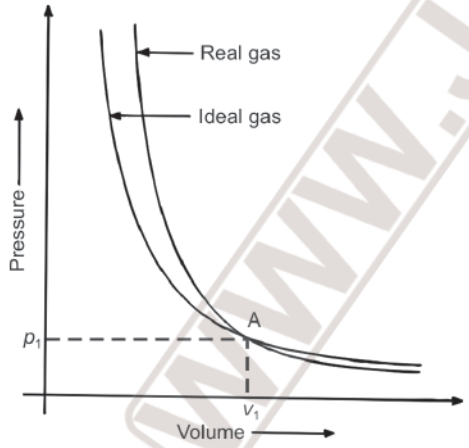
(*ii*) Interpret the behaviour of real gas with respect to ideal gas at high pressure.

(*iii*) Mark the pressure and volume by drawing a line at the point where real gas behaves as an ideal gas.

Ans. (*i*) At low pressure, the two curves almost coincide. This shows that at low pressure, the real gases show very small deviation from ideal behaviour.

(*ii*) At high pressure, the curves are far apart. This shows that real gases show large deviations at high pressure.

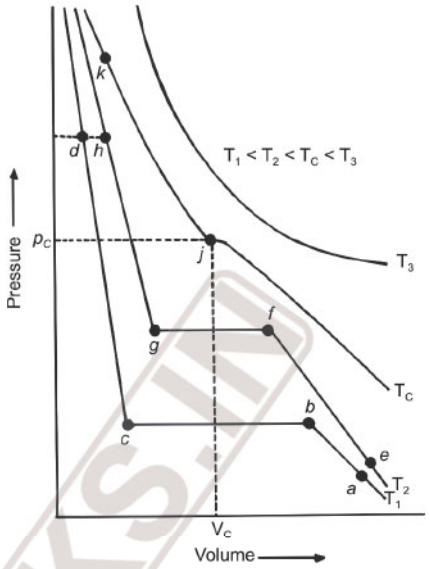
(*iii*) At point A, where the two curves intersect each other, the real gas behaves exactly like ideal gas and the pressure and volume corresponding to this point are p_1 and V_1.



Long Answer Questions *carrying 5 marks*

Q. 24. Isotherms of carbon dioxide at various temperatures are represented in figure shown below.

Answer the following questions based on this figure.



(*i*) In which state will CO_2 exist between the points *a* and *b* at temperature T_1?

(*ii*) At what point will CO_2 start liquefying when temperature is T_1?

(*iii*) At what point will CO_2 be completely liquefied when temperature is T_2.

(*iv*) Will condensation take place when the temperature is T_3?

(*v*) What portion of the isotherm at T_1 represent liquid and gaseous CO_2 at equilibrium ?

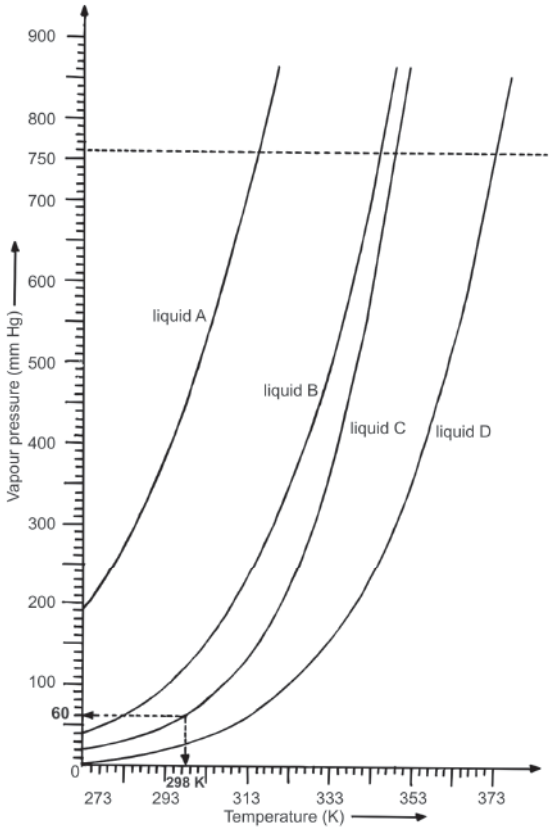
Ans. (*i*) gaseous state (*ii*) at point b

(*iii*) at point g

(*iv*) No, condensation will occur when temperature is T_3 because $T_3 > T_c$.

(*v*) between *b* and *c*.

Q. 25. The variation of vapour pressure of different liquids with temperature is shown in figure given below.



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(*i*) Calculate graphically boiling points of liquids A and B.

(*ii*) If we take liquid C in a closed vessel and heat it continuously. At what temperature will it boil ?

(*iii*) At high altitude, atmospheric pressure is low (say 60 mm Hg). At what temperature liquid D boils ?

(*iv*) Pressure cooker is used for cooking food at hill station. Explain in terms of vapour pressure why is it so ?

Ans. (*i*) Boiling point of A = 315 (approximately), B = 345 K (approximately).

(*ii*) Liquid C will not boil in a closed vessel because pressure inside keeps on changing.

(*iii*) approximately 313 K

(*iv*) A liquid boils when vapour pressure becomes equal to the atmospheric pressure. Water boils at low temperature on hills because atmospheric pressure is low. Therefore, cooking is not perfect. In a pressure cooker, the pressure inside increases and the liquid boils at a higher temperature.

Q. 26. Why does the boundary between liquid phase and gaseous phase disappear on heating a liquid upto critical temperature in a closed vessel ? In this situation what will be the state of the substance ?

Ans. *Refer Text.*

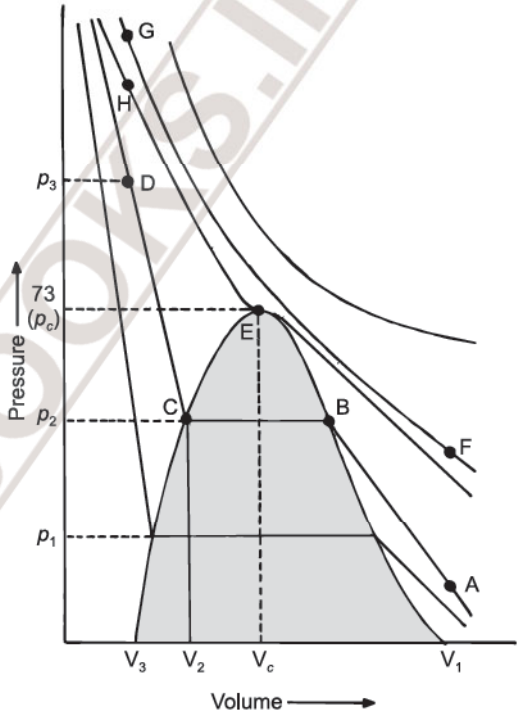
Q. 27. Why does sharp glass edge become smooth on heating it upto its melting point in a flame ? Explain which property of liquids is responsible for this phenomenon.

Ans. On heating the glass, it melts and takes up rounded shape at the edges which has minimum surface area. This is due to the property of surface tension of liquids.

Q. 28. Explain the term 'laminar flow'. Is the velocity of molecules same in all the layers in laminar flow ? Explain your answer.

Ans. *Refer Text Page 54.*

Q. 29. Isotherms of carbon dioxide gas are shown in figure given below. Mark a path for changing gas into liquid in which only one phase (*i.e*, either a gas or a liquid) exists at any time during the change. Explain how the temperature, volume and pressure should be changed to carry out the change.



Ans. Refer Text. Follow explanation of Fig. 33 (Text). Path ABCD.

QUICK MEMORY TEST

A. Say True or False

1. No gas can exist in the gaseous state at – 273°C.
2. Root mean square velocity of a gas is directly proportional to the absolute temperature of the gas.
3. Greater the critical temperature of a gas, more easily the gas can be liquefied.
4. The molar volume of any gas at 0°C and 1 bar pressure is 22400 mL.
5. N_2O and SO_2 have the same rate of diffusion under same conditions of temperature and pressure.
6. Vegetables are cooked with difficulty at a hill station.
7. Average kinetic energy of a gas is inversely proportional to the absolute temperature.
8. For an ideal gas, the value of compressibility factor is zero.
9. At the critical points, the densities of a substance in gaseous and liquid states become same.
10. When pV is plotted against p at constant temperature, a straight line parallel to pressure axis is obtained.

B. Complete the missing links

1. Average kinetic energy per molecule of a gas is related to its temperature as E_k = ...
2. The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called .....

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3. The temperature above which a gas cannot be liquefied however high the pressure may be is called..... .
4. The van der Waals constant ..... measures the forces of attraction between the molecules of a gas.
5. For H_2 and He, the compressibility factor always ..... with increase in temperature.
6. At best the real gases show the ideal behaviour at ..... pressures and ..... temperatures.
7. The ratio of average molecular kinetic energy of CO_2 (molar mass 44) to that of SO_2 (molar mass 64) at 27°C is equal to ..... .
8. For ideal gases, compressibility factor Z is equal to ..... at all conditions of temperature and pressure.
9. The numerical value of R is ..... L atm $K^{-1}mol^{-1}$ and ..... JK^{-1} mol^{-1}.
10. According to Boyle's law if pressure of a gas is reduced to 1/4, then its volume will become ..... times.

C. Choose the correct alternative

1. At constant temperature, pressure is *directly / indirectly* proportional to density of a fixed mass of gas.
2. Dispersion forces are also called *Keesom/London* forces.
3. When p is plotted against 1/V for a fixed mass of gas at a constant temperature *straight line / horizontal line* is obtained.
4. At absolute zero, kinetic energy of the gas becomes equal to *zero/one*.
5. If the gas is more compressible than expected from ideal behavior, then compressibility factor is *less / more* than one.
6. The real gases show ideal behaviour at *high / low* temperature.
7. The gases having higher values of van der Waals constant 'a' will be *easily liquefied/liquefied with difficulty*.
8. Viscosity of a liquid *decreases/increases* with rise in temperature.
9. Surface tension *decreases / increases* with increase in temperature.
10. The S.I. unit of surface tension are Nm^{-1} / Nm^{-2}.

Answers QUICK MEMORY TEST

A. Say True or False

1. True
2. **False:** Root mean square velocity is directly proportional to the square root of the absolute temperature.
3. True
4. **False:** At 0°C and 1 bar pressure, molar volume of a gas is equal to 22700 mL.
5. **True:** because these have same molar mass (44 g mol^{-1})
6. True
7. **False:** Average kinetic energy is directly proportional to temperature.

$$\overline{KE} = \frac{3}{2}kT.$$

8. **False:** For an ideal gas, Z = 1.
9. True
10. True.

B. Complete the missing links

1. $\frac{3}{2}kT$.
2. Boyle temperature
3. Critical temperature
4. a
5. increases
6. low, high
7. 1
8. one
9. 0.0821, 8.314
10. 4

C. Choose the correct alternative

1. directly
2. London
3. Straight line
4. zero
5. less
6. high
7. easily liquefied
8. decreases
9. decreases
10. Nm^{-1}.

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. If the molecular speeds of gaseous molecules are analogous to those of rifle bullets, why is the odour of the gaseous molecules not detected so fast ?

Ans. Even though the speeds of gaseous molecules are analogous to those of rifle bullets, these do not move in a straight path like bullets. Therefore, the molecules undergo collisions with one another at a very fast rate and follow zig-zag path. As a result, the odour cannot be detected at the same speed at which the molecules move.

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Q. 2. Distinguish between the total kinetic energy of a molecule and its translational kinetic energy. For what type of gas molecules are they same ?

Ans. The total kinetic energy of a molecule includes the translational kinetic energy, rotational kinetic energy and vibrational kinetic energies.

For monoatomic gases both rotational and vibrational kinetic energies are zero. Therefore, for these, total kinetic energy is equal to translational kinetic energy.

Q.3. Wet cold weather is much more penetrating than dry cold weather. Explain.

Ans. The average molecular mass of dry air is about 29.16 as calculated below :

$$\text{Average molecular mass of air} = \frac{71\times 28 + 29\times 32}{100}$$

$$= 29.16$$

However, average molecular mass of moist air is less than 29.16 because of the presence of water vapours (mol. mass = 18) as

$$\text{Average molecular mass of moist air} = \frac{\%\text{ of dry air} \times 29.16 + \%\text{ of water vapours}\times 18}{100}$$

Since the penetration power is inversely proportional to molecular mass, the wet cold weather will be much more penetrating than dry cold weather.

Q.4. CO_2 is heavier than N_2 and O_2 gases present in the air but it does not form the lower layer of the atmosphere. Explain ?

Ans. Gases have the property of diffusion which is independent of the force of gravitation. Due to diffusion, the gases mix into each other and remain almost uniformaly distributed in the atmosphere.

Q.5. Explain why Boyle's law cannot be used to calculate the volume of a real gas when it is converted from its initial state to final state by an adiabatic expansion.

Ans. During adiabatic expansion, temperature is lowered and therefore, Boyle's law cannot be applied.

Q.6. Write expression for Boyle's temperature and critical temperature in terms of van der Waals constants. Which one is larger for a particular gas ?

Ans. Boyle temperature, $T_B = \frac{a}{bR}$

Critical temperature, $T_C = \frac{8a}{27\,R_b}$

Thus, $T_B > T_C$

Q.7. A given mass of a gas collected over water at 25°C has a pressure of 500 mm Hg. Calculate the pressure if its volume is reduced to half of its original volume (aqueous tension at 25°C = 24 mm of Hg).

Ans.

Initial conditions	*Final conditions*
$V_1 = V$ (Suppose)	$V_2 = \frac{V}{2}$
$p_1 = 500 - 24 = 476$ mm	$p_2 = ?$

According to Boyle's law (temperature is constant)

$$p_1V_1 = p_2V_2$$

$$\therefore \quad p_2 = \frac{p_1V_1}{V_2} = \frac{476\times V}{V/2}\ \text{m} = 2\times 476\ \text{mm}$$

$$= 952\ \text{mm}.$$

This corresponds to the pressure of the dry gas. Since the gas is collected over water, its pressure will be

$$p = 952 + \text{aqueous tension}$$

$$= 952 + 24 = 976\ \text{mm of Hg}.$$

Q.8. A gas is enclosed in a room. The temperature, pressure, density and number of moles respectively are t°C, p atm, d g cm^{-3} and n moles.

(*a*) What will be the pressure, temperature, density and number of moles in each compartment if room is partitioned into four equal compartments ?

(*b*) What will be the values of pressure, temperature, density and number of moles in each compartment if the walls between the two compartments (say 1 and 2) are removed ?

(*c*) What will be the values of pressure, temperature, density and number of moles, if an equal volume of gas at pressure p and temperature t is let inside the same room ?

Ans. (*a*)

(*i*) Pressure in each compartment is same, p. Because of partition, volume of each compartment becomes 1/4 and the number of molecules also become 1/4.

(*ii*) Temperature will remain same (t°C).

(*iii*) Density will remain same (d g cm^{-3}).

(*iv*) The number of moles in each compartment will be $n/4$.

(*b*) (*i*) Pressure will remain same (p atm)

(*ii*) Temperature will remain same (t°C)

(*iii*) Density will remain same (d g cm^{-3})

(*iv*) the number of moles in each compartment will be $n/2$.

(*c*) (*i*) Pressure will be doubled ($2p$ atm)

(*ii*) Temperature will remain same.

(*iii*) Density will be doubled ($2d$ g cm^{-3})

(*iv*) Number of moles will be doubled, *i.e.* $2n$.

Q.9. When 2 g of gas A is introduced into an evacuated flask kept at 25°C, the pressure is found to be 1 atm. If 3 g of another gas B is then added to the same flask the total pressure becomes 1.5 atm at the same temperature. Assuming ideal behaviour of gases, calculate the ratio of molecular weights $M_A : M_B$.

Ans. According to ideal gas equation,

$$pV = nRT$$

$$\text{or} \quad pV = \frac{mRT}{M} \qquad \text{or} \qquad M = \frac{m}{pV}RT \quad n = \frac{m}{M}$$

Let the molecular weight of A and B be M_A and M_B respectively.

$$M_A = 2\,\frac{RT}{1\times V} \quad \text{and} \quad M_B = \frac{3\,RT}{0.5\times V}$$

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or $\frac{M_A}{M_B} = \frac{2}{3} \times 0.5 = \frac{1}{3}$

$\therefore$ $M_A : M_B = \mathbf{1 : 3.}$

Q.10. A balloon of diameter 20 m weighs 100 kg. Calculate the pay load if it is filled with He at 1.1 atm and 27°C. Density of air is 1.2 kg m^{-3} (R = 0.082 dm^3 atm K^{-1} mol^{-1}).

Ans. Volume of balloon,

$$V = \frac{4}{3}\pi r^3$$

r = 10 m

$\therefore$ $V = \frac{4}{3} \times 3.14 \times (10)^3 = 4187 \text{ m}^3$

Mass of displaced air = 4187 m^3 × 1.2 kg m^{-3}
= 5024.4 kg

Moles of gas present, $n = \frac{pV}{RT}$

$= \frac{1 \times 4187 \times 10^3}{0.082 \times 298}$

$= 170.2 \times 10^3$ mol

Mass of He present = $170.2 \times 10^3 \times 4$
= 680.8×10^3 g
= 680.8 kg

Mass of filled balloon = 100 + 680.8 = 780.8 kg

Pay load = Mass of displaced air – Mass of balloon
= **5024.4 –780. 8 = 4243.6 kg**

Q.11.At 27°C, hydrogen is leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure as that of H_2 leaked through the same hole for 20 minutes. After the effusion of gases the mixture exerts a pressure of 6 atm. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 litre, what is the molecular weight of the unknown gas.

Ans. Total volume of effused gas is 3 litre and its pressure at 27°C is 6 atm. No. of moles of effused mixture may be calculated as

$$n = \frac{pV}{RT} = \frac{6 \times 3}{0.0821 \times 300}$$

$= 0.7308$

Moles of H_2 = 0.7

$\therefore$ Moles of unknown gas = 0.7308 – 0.7
= 0.0308 moles

Rate of effusion of H_2, $r_{H_2} = \frac{0.7}{20}$

Rate of effusion of unknown gas, $r_g = \frac{0.0308}{20}$

According to Graham's law,

$$\frac{r_{H_2}}{r_g} = \frac{0.7/20}{0.0308/20} = \sqrt{\frac{M_g}{M_{H_2}}}$$

$\therefore$ $\frac{0.7}{0.0308} = \sqrt{\frac{M_g}{2}}$

$\therefore$ $M_g = \left(\frac{0.7}{0.0308}\right)^2 \times 2 = \mathbf{1033.}$

Q.12. 20 dm^3 of SO_2 diffuse through a porous partition in 60s. What volume of O_2 will diffuse in 30s under similar conditions ?

Ans. Rate of diffusion = $\frac{\text{Vol. of gas diffused}}{\text{Time taken for diffusion}}$

$r_{so_2} = \frac{20}{60}$ and $r_{(O_2)} = \frac{V_{O_2}}{30}$

According to Graham's law of diffusion

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \text{ or } \frac{r_{so_2}}{r_{o_2}} = \sqrt{\frac{M_{o_2}}{M_{so_2}}}$$

$$\frac{20/60}{V_{O_2}/30} = \sqrt{\frac{32}{64}}$$

$\therefore$ $V_{O_2} = \frac{1}{3} \times 30 \times \sqrt{2} = 14.1 \text{ dm}^3$.

Q.13. An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g mL^{-1} and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molecular weight of the gas.

Ans. Weight of liquid = 148 – 50 = 98 g

Density of liquid = 0.98 g ml^{-1}

$\therefore$ Volume of liquid = $\frac{98}{0.98}$ = 100 ml

Wt. of gas = 50.5 – 50.0 = 0.5 g

Volume = $\frac{100}{1000}$ L, P = 1 atm, T = 300 K

$pV = nRT$ or $pV = \frac{W}{M}RT$

$$\frac{1 \times 100}{1000} = \frac{0.5}{M} \times 0.082 \times 300$$

$\therefore$ $M = \mathbf{123.15 \text{ g mol}^{-1}}$.

Q.14. A glass bulb contains 2.24 L of H_2 and 1.12 L of D_2 at S.T.P. It is connected to a fully evacuated bulb by a stop cock with a small opening. The stop cock is opened for some time and then closed. The first bulb now contains 0.10 g of D_2. Calculate the percentage composition by weight of the gases in the bulb.

Ans. Calculation of amount of H_2 in the bulb

22.4 L of H_2 at S.T.P. weigh = 2 g

2.24 L of H_2 at S.T.P. weigh = $\frac{2 \times 2.24}{22.4} = 0.2$ g

Similarly,

Amount of D_2 in bulb = $\frac{1.12 \times 4}{22.4} = 0.2$ g

Amount of D_2 left after opening the stop cock = 0.10 g

$\therefore$ Amount of D_2 diffused = 0.2 – 0.10 = 0.1 g

Volume of O_2 diffused = $\frac{0.1 \times 22.4}{4} = 0.56$ L

Let the volume of H_2 diffused from first bulb = x L

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According to Graham's law,

$$\text{rate, } r = \frac{V}{t}$$

$$r_{H_2} = \frac{x}{t} \text{ and } r_{D_2} = \frac{0.56}{t}$$

$$\therefore \quad \frac{r_{H_2}}{r_{D_2}} = \frac{\frac{x}{t}}{\frac{0.56}{t}}$$

Now, $$\frac{\frac{x}{t}}{\frac{0.56}{t}} = \sqrt{\frac{M_{D_2}}{M_{H_2}}} = \sqrt{\frac{4}{2}}$$

$$\therefore \quad x = 0.56 \times \sqrt{2}$$

$$= 0.56 \times 1.414 = 0.79 \text{ L}$$

Amount of D_2 in the second bulb = 0.1 g

Amount of H_2 in the second bulb $= \frac{0.79 \times 2}{22.4}$

$= 0.0707$ g

Total amount of gases in the second bulb

$= 0.1 + 0.0707$

$= 0.1707$ g

$$\% \text{ of } H_2 \text{ gas} = \frac{0.0707 \times 100}{0.1707} = \mathbf{41.2\%}$$

$$\% \text{ of } D_2 \text{ gas} = \frac{0.1 \times 100}{0.1707} = \mathbf{58.8\%}.$$

Q.15. Calculate the total pressure in a 10 L cylinder which contains 0.4 g of helium, 1.6 g of oxygen and 1.4 g of nitrogen at 27°C. Also calculate the partial pressure of helium gas in the cylinder. Assume ideal behaviour for gases (R = 0.082 L atm K^{-1} mol^{-1}).

Ans. $$\text{Moles of helium} = \frac{0.4}{4} = 0.1$$

$$\text{Moles of oxygen} = \frac{1.6}{32} = 0.05$$

$$\text{Moles of nitrogen} = \frac{1.4}{28} = 0.05$$

Total moles $= 0.1 + 0.5 + 0.5 = 0.2$ mole

Volume of gaseous mixture = 10 L

Temperature = 27 + 273 = 300 K

R = 0.082 L atm mol^{-1} K^{-1}

Now, $pV = nRT$

or $$p = \frac{nRT}{V}$$

$$= \frac{0.2 \times 0.082 \times 300}{10}$$

$$= \mathbf{0.492 \text{ atm}}.$$

Partial pressure of helium = Mole fraction of He × p

$$= \frac{0.1}{0.2} \times 0.492$$

$$= \mathbf{0.246 \text{ atm}}.$$

Q.16. A fluoride of phosphorus in the gaseous state was found to diffuse more slowly by a factor of 2.12 than nitrogen under the same conditions. Calculate the molecular weight of this fluoride. If it contains only one phosphorus atom, write its molecular formula.

Ans. According to Graham's law,

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

M_2, Mol. wt. of N_2 = 28

M_1, Mol wt. of fluoride = ? M (say)

$$\frac{r_1}{r_2} = \sqrt{\frac{28}{M}}$$

Now, $$\frac{r_1}{r_2} = \frac{1}{2.12}$$

$$\frac{1}{2.12} = \sqrt{\frac{28}{M}}$$

or $$\frac{28}{M} = \frac{1}{(2.12)^2}$$

$$\therefore \quad M = (2.12)^2 \times 28 = \mathbf{126}$$

Let formula of fluoride = PF_x

$$31 + 19x = 126$$

$$19x = 126 - 31 = 95$$

$$\therefore \quad x = \frac{95}{19} = 5$$

$\therefore$ Molecular formula = $\mathbf{PF_5}$.

Q.17. A mixture in which the mole ratio of H_2 and O_2 is 2 : 1 is used to prepare water by the reaction :

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$

The total pressure in the container is 0.8 atm at 20°C before the reaction. Calculate the final pressure at 120°C after reaction assuming 80% yield of water.

Ans.

	$2H_2(g)$	$+ O_2(g)$	$\longrightarrow 2H_2O(g)$
Initially moles	2	1	0
Moles at equiv.	2 – 1.6 = 0.4	1 – 0.8 = 0.2	1.6

Total moles after reaction = 0.4 + 0.2 + 1.6 = 2.2

Let the initial pressure at 20°C = P_1

Pressure at 120°C = P_2

According to Gay-Lussac's Law

$$\frac{p_1}{p_2} = \frac{T_1}{T_2} \quad \text{or} \quad \frac{0.8}{p_2} = \frac{293}{393}$$

or $$p_2 = \frac{0.8 \times 393}{293} = 1.073 \text{ atm.}$$

Now, $$\frac{\text{Initial moles}}{\text{Moles after equiv.}} = \frac{\text{Initial pressure}}{\text{Pressure after equiv.}}$$

$$\frac{3}{2.2} = \frac{1.073}{p_{\text{equiv.}}}$$

or $$p_{\text{equiv.}} = \frac{1.073 \times 2.2}{3} = \mathbf{0.787 \text{ atm.}}$$

Q.18. A plant virus is found to consist of uniform cylindrical particles of 150Å diameter and 5000Å long. The specific volume of the virus is 0.75 cm^3/g. If the virus is considered to be a simple particle, find its molecular weight.

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Ans. Radius of virus $(r) = \frac{150}{2} = 75\text{Å}$

$= 75 \times 10^{-8}$ cm

$h = 5000\text{Å} = 5000 \times 10^{-8}$ cm

Volume of one virus particle $= \pi r^2 h$

$$= \frac{22}{7} \times \left(75 \times 10^{-8}\right)^2 \times \left(5000 \times 10^{-8}\right)$$

$$= 8.84 \times 10^{-17}\ \text{cm}^3$$

$$\text{Mass of one virus particle} = \frac{\text{Volume}}{\text{Specific volume}}$$

$$= \frac{8.84 \times 10^{-7}}{0.75}$$

$$= 1.179 \times 10^{-16}\ \text{g}$$

Molecular mass = Mass of a virus particle × Avogadro number

$= 1.179 \times 10^{-16} \times 6.023 \times 10^{23} = \mathbf{7.10 \times 10^7\ g\ mol^{-1}}$

Q.19. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pin hole whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm. takes 57 s to diffuse through the same hole. Calculate the molecular formula of the compound.

Ans. Rate of diffusion,

$$r = \frac{\text{K}.p}{\sqrt{\text{M}}}$$

$$r_{N_2} = \frac{1}{38}\ \text{mol s}^{-1},$$

$$r_x = \frac{1}{57}\ \text{mol s}^{-1}$$

For N_2, $\quad \frac{1}{38} = \frac{\text{K} \times 0.8}{\sqrt{28}} \quad ...(i)$

For unknown gas, $\quad \frac{1}{57} = \frac{\text{K} \times 1.6}{\sqrt{\text{M}_x}} \quad ...(ii)$

Dividing (i) by (ii)

$$\frac{1}{38} \times \frac{57}{1} = \frac{0.8}{1.6} \times \sqrt{\frac{\text{M}_x}{28}}$$

$$\frac{3}{2} = \frac{1}{2} \times \left(\frac{\text{M}_x}{28}\right)^{\frac{1}{2}}$$

or $\quad \text{M}_x = 9 \times 28 = 252\ \text{g mol}^{-1}$

Molecular mass of compound of Xe and F = 252. Let the formula be MF_x so that

$$131 + x \times 19 = 252$$

$$19x = 252 - 131 = 121$$

$$x = \frac{121}{19} = 6.36 \text{ or } \approx 6$$

$\therefore$ Molecular formula = $\mathbf{XeF_6}$.

Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. What is the value of temperature absolute zero in Celsius scale ? How are the two scales related ?
2. What do you understand by standard temperature and pressure ?
3. Define Boyle's law and Charles' law.
4. Write van der Waal's equation for n moles of a gas.
5. Gases do not settle at the bottom of a container. Explain.
6. Name and state the law governing the expansion of gases when they are heated or cooled at constant pressure.
7. How many elements exist as gases in periodic table under normal conditions of temperature and pressure ?
8. What is the effect of temperature on the vapour pressure of a liquid ?
9. What is the effect of pressure on the boiling point of a liquid ?
10. Arrange solid, liquid and gas in order of molecular energy giving reasons.
11. What is the ratio of root mean square speed and most probable speed ?
12. Will water boil at higher temperature at sea level or at the top of mountains ?
13. Define critical temperature.
14. Arrange the following liquids in the increasing order of their normal boiling points :

    $C_2H_5OH, (C_2H_5)_2O, H_2O$.
15. Liquids like acetone and ether are kept in cool place. Why ?
16. Why are hydrogen and helium not liquefied at room temperature ?
17. Warm water evaporates faster than cold water. Explain.
18. Cooling is caused during evaporation. Why ?
19. What is compressibility factor ? What is its value for an ideal gas ?
20. A rubber balloon permeable to hydrogen in all its isotopic forms is filled with deuterium (D_2) and then placed in a box containing pure hydrogen. Will the balloon expand or contract or remains as it is ?
21. What would be the SI unit for the quantity, pV^2T^2/n ?

    N.C.E.R.T.
22. In terms of Charles' law explain why –273°C is the lowest possible temperature. ***N.C.E.R.T.***
23. What is meant by supercritial fluid ?
24. Critical temperatures for CO_2 and methane are 31.1°C and –81.9°C respectively. Which of these has stronger intermolecular forces and why ? ***N.C.E.R.T.***
25. What happens when a liquid a heated to the critical temperature of its vapours ?
26. Why does a liquid boil at low temperature at the top of a mountain than at a sea level ?
27. What is the SI unit of coefficient of viscosity ? How is it related to poise ?
28. Write equation of state for real gases.

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29. What is universal gas constant ? What is its value in SI units ?

30. What is the effect of temperature on (*i*) surface tension (*ii*) viscosity ?

Short Answer Questions *carrying 2 or 3 marks*

1. How will you account for Charles' law on the basis of kinetic molecular theory of gases ?

2. State and explain Boyle's law and Charles' law. Derive gas equation from these laws.

3. On the basis of intermolecular energy and thermal energy explain why ?
(*i*) a solid has rigidity but a liquid does not have rigidity.
(*ii*) gases have high compressibility but solids and liquids have poor compressibility.

4. Establish the relationship between temperature, pressure and volume of a given mass of a gas.

5. Write short notes on : Dalton's law of partial pressures and its applications.

6. Deduce the gas equation $pV = nRT$ from different gas laws.

7. Discuss the significance of gas constant R. Calculate its value in joules K^{-1} mol^{-1}.

8. Why is air at sea level denser than air at high altitudes ?

9. Define :
(*i*) Absolute zero
(*ii*) Standard temperature and pressure.

10. Derive the relation between density and molar mass of a gas.

11. Using the equation of state, $pV = nRT$, show that at a given temperature density of a gas is proportional to gas pressure p.

12. Justify the statement 'volume of a gas at a constant pressure decreases if its temperature is decreased'.

13. What do you understand by the terms ideal gas and real gas ? Explain.

14. Comment on the statement that all gases behave ideally at low pressures and high temperatures.

15. Comment on the statement that liquid state is an intermediate state between the gaseous state and the solid state.

16. Would you expect surface tension and viscosity of a liquid to increase or decrease with increasing temperature ? Explain.

17. Why do gases deviate from ideal behaviour ? Write van der Waal's equation for real gases stating significance of each term involved.

18. Explain why ice has sharp melting point whereas glass melts over a range of temperature.

19. Explain the physical significance of van der Waals parameters.

20. Explain :
(*i*) The boiling point of a liquid rises on increasing pressure.
(*ii*) Liquids like ether and acetone are kept in cool places.

21. Why does the boiling temperature of liquid becomes constant once it starts boiling ?

22. Explain the term viscosity of a liquid. How does it vary with temperature ?

23. If you pour ether on your hand, it feels much colder than if you pour water of the same temperature. Explain.

24. What do you understand by surface tension of a liquid ? How does it vary with temperature ?

25. What is critical temperature ? What is its importance in liquefaction of gases ?

26. State and explain Dalton's law of partial pressures. What is its utility ?

27. State Boyle's and Charles' laws. How are they combined to give general gas equation ?

28. Why are certain liquids viscous while certain others are moblile ?

29. Define the following :
(*i*) Critical temperature (*ii*) Critical volume
(*iii*) Critical pressure

30. How does van der Waals' equation of state account for the exceptional behaviour of hydrogen and helium ?

31. Explain Andrew's isotherms for carbon dioxide.

32. What is viscosity and coefficient of viscosity ? What are SI units of coefficient of viscosity ?

33. Explain how does surface tension account for
(*i*) Capillary action of liquids
(*ii*) Spherical shape of liquid drops

34. What do you understand by isobars, isotherms and isochores ? Explain.

35. Explain the following laws :
(*i*) Gay Lussac's law
(*ii*) Avogadro's law

36. Explain : a gas can be changed into liquid or a liquid into a gas by a process in which a single phase is always present.

37. Comment on the continuity between gaseous and liquid state.

38. What is the significance of van der Waals constants ? Out of N_2 and NH_3 which one will have (*i*) larger value of a (*ii*) larger value of b.

39. Derive the relationship between partial pressure of gas and total pressure of gas and mole fraction.

40. What is compressibility factor ? How does it help to account for nature of a gas ?

41. One of the assumptions of kinetic theory of gases is that there is no force of attraction between the molecules of a gas. State and explain the evidence that shows that the assumption is not applicable for real gases.

42. The relation between pressure exerted by an ideal gas (p_{ideal}) and observed pressure (p_{real}) is given by the equation

$$p_{ideal} = p_{real} + \frac{an^2}{V^2}$$

(*i*) If pressure is taken in Nm^{-2}, number of moles in mol and volume in m^3, calculate the unit of 'a'.
(*ii*) What will be the unit of 'a' when pressure is in atmosphere and volume in dm^3?

43. One of the assumptions of kinetic theory of gases states

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that "there is no force of attraction between the molecules of a gas." How far is this statement correct? Is it possible to liquefy an ideal gas? Explain.

Long Answer Questions *carrying 5 marks*

1. What are the main postulates of kinetic theory of gases ? Explain Boyle's law on the basis of kinetic theory.
2. Deduce the gas equation pV = nRT from gas laws. Discuss the significance of gas constant R. Calculate its value in Joules K^{-1} mol^{-1}.
3. What is an ideal gas ? Why do real gases deviate from ideal behaviour ? Derive the Van der Waals' equation.
4. Define Charles' law and Dalton's law of partial pressure. How does kinetic molecular theory of gases account for these laws ?
5. What is liquid state of matter ? Discuss the following properties of liquids :
   (*i*) Evaporation (*ii*) Boiling point
   (*iii*) Viscosity (*iv*) Surface tension.
6. Compare the three states of matter in terms of size and volume. Justify the statement that liquid state is intermediate state between solid state and gaseous state.
7. What is liquefaction of a gas ? Discuss Andrew's isotherms for carbon dioxide and important conclusions.
8. What are critical constants ? What are their significances?

Numerical Problems *carrying 5 marks*

1. What is the volume of a sample of oxygen at a pressure of 2.50 bar, if its volume is 3.15 L at 1.0 bar ? (Assume constant temperature).
2. At 450°C and 723 mm pressure, 3.2 g of sulphur vapours occupy a volume of 780 mL. What is the molecular formula under these conditions ?
3. A 2L vessel contains oxygen at a pressure of 380 mm Hg at 27°C. 1.40 g of N_2 gas is introduced in the vessel. Will the pressure of gaseous mixture increase or decrease and to what extent?
4. 250 mL of hydrogen measured at 750 mm of Hg have to be compressed into a vessel of 50 mL capacity at a constant temperature. Calculate the pressure required to do so.
5. The mass of 500 mL of hydrogen gas at a pressure of 1 bar and at temperature of 300 K was found to be 4.09×10^{-2} g. Calculate the molar mass of hydrogen.
6. At room temperature, ammonia gas at 1 atm pressure and HCl gas at pressure P atm are allowed to effuse through identical pin holes from opposite ends of a glass tube of 1 metre length and uniform area of cross-section. NH_4Cl is first formed at a distance of 60 cm from the end through which HCl gas was sent in. Calculate the value of P.
7. A 1.00 L evacuated flask is to be filled with CO_2 gas at 300°C and a pressure of 500 mm Hg by placing a piece of dry ice, CO_2 (s) in the flask. What mass of dry ice should be used ?
8. A gas mixture of 3.0 L of propane and butane on complete combustion at 27°C produced 10.0 L of CO_2. Find out the composition of the gas mixture.
9. 0.64 g of an oxide of sulphur occupies 0.224 L at 2 bar and 273°C. Identify the compound. Also find out the mass of one molecule of the gas.
10. A mixture of nitrogen and hydrogen gas has density 0.505×10^{-3} g cm^{-3} at 293 K and 750 mm Hg pressure. What per cent of the mass is nitrogen ?
11. A toy balloon blown up at 5°C has a volume of 480 ml. At this stage, the balloon is distended to 7/8th of its maximum stretching capacity.
    (*i*) Will the balloon burst if it is brought to a room having temperature 30°C ?
    (*ii*) Calculate the temperature at which the balloon will burst.
12. A mixture of H_2 and N_2 weighing 0.116 g is collected over water at 50°C and occupies a volume of 275 ml when the total pressure is 1.0 atm. Calculate the composition of the dry mixture in mole per cent. The vapour pressure of water at 50°C is 92.5 torr.
13. The critical constants for water are 374°C, 218 bar and 0.0566 L mol^{-1}. Calculate a and b constants.

Hints & Answers *for* Revision Exercises

Very Short Answer Questions

1. –273°C, K = 273 + °C
2. Standard temperature and pressure are 0°C or 273 K and 1 atm respectively.
4. $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$ is van der Waals' equation for n moles of a gas.
6. Charles' law
7. 11 Elements
8. Vapour pressure increases with rise in temperature.
9. Boiling point increases as prevailing pressure increases.
10. Solid < liquid < gas
11. Most probable speed : r.m.s. speed = 1:1.224.
12. Water will boil at higher temperature at sea level.
14. $(C_2H_5)_2O < C_2H_5OH < H_2O$.

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19. Compressibility factor, $Z = \frac{pV}{nRT}$. For ideal gas Z = 1.

20. Balloon will expand because rate of diffusion of H_2 is greater than that of D_2.

25. Meniscus between liquid and vapour disappears.

26. Atmospheric pressure is low at a mountain.

27. SI unit = kg m^{-1} s^{-1}

1 poise = $\frac{1}{10}$ th of SI unit.

28. van der Waals equation,

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

29. 8.314 JK^{-1} mol^{-1}

30. Both decreases with increases in temperature.

Short Answer Questions

16. With increasing temperature surface tension and viscosity decrease.

Numerical Problems

1. Applying Boyle's law

$$p_1 V_1 = p_2 V_2 \text{ (at constant T)}$$

or $$V_2 = \frac{p_1 V_2}{p_2}$$

$\therefore$ $$V_2 = \frac{1.0 \times 3.15}{2.50} = 1.26 \text{ L.}$$

2. $T = 450 + 273 = 273$ K

$p = 72/760$ atm

Mass of sulphur = 3.2g, V = 780 mL

$$M = \frac{mRT}{pV}$$

$$M = \frac{3.2 \times 82.1 \times 723}{723 \times 760 \times 780} = 256$$

Now, Atomic weight of sulphure = 32

No, of sulphur atoms in molecule = $\frac{256}{32} = 8$

Molecular formula = $\mathbf{S_8}$.

3. V = 2 L, p = 380/760 = 0.5 atm, T = 273 + 27 = 300 K

$pV = nRT$

$$n = \frac{pV}{RT}$$

Moles of oxygen present, $n = \frac{0.5 \times 2}{0.082 \times 300} = 0.041$ mol

Moles of nitrogen added = $\frac{1.40}{28} = 0.05$ mol

Total moles of gases present = 0.041 + 0.05 = 0.091

Now, pressure of gaseous mixure,

$$p = \frac{nRT}{V} = \frac{0.091 \times 0.082 \times 300}{2} = 1.12$$

$\therefore$ Pressure will increase to **1.12 atm.**

4. Since temperature is constant

$p_1 V_1 = p_2 V_2$

$p_2 = ?$

$V_2 = 50$ *ml*

$$p_2 = \frac{p_1 V_1}{V_2} = \frac{750 \times 250}{50} = 3470 \text{ mm Hg}$$

5. $pV = nRT$ or $pV = \frac{m}{M}RT$ or $M = \frac{mRT}{pV}$

Here p = 760 mm Hg = atm, T = 300,

V = 500 cm^3 = $\frac{500}{1000}$ L,

R = 0.082 $cm^3 = K^{-1}$, $m = 4.09 \times 10^{-2}$ *g*

$\therefore$ $M = \frac{4.09 \times 0.082 \times 300}{1 \times 500/1000}$ = **2.01.**

6. Since pressure of gases are differnet, and the temperatrue is constant, the rate of diffusion of gases is also directly proprotional to their pressure.

$$\frac{r_1}{r_2} = \frac{p_1}{p_2} = \sqrt{\frac{M_1}{M_2}}$$

For ammonia : p_1 = atm

$m_1 = 14$

For hydrogen chloride : $p_2 = p$ (say)

$m_2 = 36.5$

$r_1 = \frac{40}{t}$, $r_2 = \frac{60}{t}$

$$\frac{\frac{40}{t}}{\frac{60}{t}} = \frac{1}{p}\sqrt{\frac{36.5}{17}}$$

$$p = \frac{60}{40}\sqrt{\frac{36.5}{17}}$$

7. $pV = nRT$ or $pV = \frac{m}{M}RT$

$p = \frac{500}{760}$ atm,

V = 1.0 L, T = 300 + 273 = 573 K,

M = 44

$\therefore$ $$m = \frac{pVM}{RT} \quad \frac{500}{760} \times 1.0 \times 44 \quad \frac{}{0.082 \times 573}$$

= **0.616 g.**

8. Let the volume of propane = V litre

Volume of butane = (3 – V) litre

$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$

V litre 3 V litre

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$$C_4H_{10} + \frac{13}{2} O_2 \longrightarrow 4CO_2 + 5H_2O$$

(3 – V) litre 4 (3 – V) litre

Total voplume of CO_2 produced = 10 L

$\therefore$ $3V + 4(3 - V) = 10$

or $3V - 4V = 10 - 12$

or $V = 2$ L

Volume of propane = 2 L,

Voluem of butane = 3 – 2 = 1 L

% of propane = $\frac{2}{3} = 66.7$

% of butane = $\frac{1}{3} = 33.3$.

9. $pV = nRT$

or $pV = \frac{m}{M} RT$

or $M = \frac{mRT}{pV}$

$p = 2$ atm, $V = 0.224$ L

$T = 273 = 546$,

$R = 0.082$ L atm mol^{-1} K^{-1},

$m = 0.64$ g

$$M = \frac{0.64 \times 0.082 \times 546}{2 \times 0.224}$$

$= 63.96 \approx 64$

The possible oxide is SO_2

(molar mass $32 + 2 \times 16 = 64$)

$$\text{Mass of 1 molecule of oxide} = \frac{\text{Molar mass}}{\text{Avogadro number}}$$

$$= \frac{64}{6.023 \times 10^{23}} = \mathbf{1.063 \times 10^{22} g.}$$

10. Density = 0.505×10^{-3} g cm^{-3}

or $0.505 \times 10^{-3} \times 1000$ g $L^{-1} = 0.505$ gL^{-1}.

Let us first calculate moles of mixure

$$n = \frac{nV}{RT} = \frac{750/760 \times 1}{0.082 \times 293}$$

$= 0.041$ mol

Let the mixture contains nitrogen = x mol

Moles of hydrogen = $(0.041 - x)$ mol

Mass of x moles of $N_2 = 28x$

Mass of $(0.041 - x)$ moles of $H_2 = 2(0.041 - x)$

Total mass $= 28x + 2(0.041 - x) = 0.505$g

$26x = 0.505 - 0.082 = 0.423$

or $x = \frac{0.423}{26} = 0.0163$

Mass of $N_2 = 0.0163 \times 28 = 0.4564$g

$$\% \text{ of } N_2 = \frac{0.4564}{0.505} \times 100 = 90.37\%$$

11. Since the pressure remains constant, Charles law is applicable,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

or $V_2 = \frac{V_1 T_2}{T_1}$

$$V_2 = \frac{480 \times 303}{278}$$

or $V_2 = \mathbf{523\ mL}$

Maximum volume upto which the balloon can be blown without bursting

$$= \frac{480 \times 8}{7} = 548.6 \text{ mL}$$

$\therefore$ Balloon will not burst in a room at 30°C.

(*ii*) Let us calculate the temperature at which volume becomes 548. 6 ml (V_2)

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

or $T_2 = \frac{V_2 T_1}{V_1}$

$$T_2 = \frac{548.6 \times 278}{480} = 317.7 \text{ K}$$

$\therefore$Balloon will burst at **317.7 K or 44.7° C.**

12. Let the mass of H_2 in the mixture = xg

Mass of $N_2 = (0.116 - x)$g

Let us first calculate total moles of N_2 and H_2 present

V = 275 mL T = 273 + 50 = 323 K

$p = p_{total} - pH_2O = 760 - 90.5 = 667.5$ torr.

Now, $pV = nRT$ or $n = \frac{pV}{RT}$

$$n = \frac{667.5/760 \times 275}{82.1 \times 323}$$

$= 0.00911$

Now, $\frac{x}{2} + \frac{0.116 - x}{28} = 0.00911$

Solving $x = 0.0107$

Moles of $H_2 = \frac{0.0107}{2} = 0.00535$

Mol % of $H_2 = \frac{0.00535}{0.00911} \times 100 = 58.7\%$

Mol% of $N_2 = 100 - 58.7 = \mathbf{41.3\%}$

13. $p_c = \frac{a}{27b^2}$

or $L = \frac{8a}{27Rb}$

$V_c = 3b$ or $b = \frac{8a}{27Rb}$

$$= \frac{0.0566}{3} = \mathbf{0.0189}$$

Now $p_c = \frac{a}{27b^2}$

or $a = p_c \times 27b^2 = 218 \times 27 \times (0.0189)^2$

$= \mathbf{2.102}$

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Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

MOLECULAR COLLISIONS, COLLISION FREQUENCY AND MEAN FREE PATH

Collision frequency. The total number of collisions taking place in a unit volume per second is called the collision frequency (Z). For binary collisions,

$$Z = \frac{1}{\sqrt{2}}\pi v\sigma^2N^2$$

where v = average velocity, σ = molecular diameter and N = number of molecules per unit volume.

At a particular temperature, $Z \propto p^2$

At a particular pressure, $Z \propto \frac{1}{T^{3/2}}$

Mean free path. It is the average distance travelled by a molecule between any two successive collisions. It is denoted by λ and

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2N}$$

Mean free path is related to temperature and pressure as,

$\lambda \propto \frac{1}{p}$ at constant T and $\lambda \propto T$ at constant p.

OBJECTIVE TYPE QUESTIONS

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Gas Laws and Ideal Gas Equation

A1. Measurement of the amount of dry gas collected over water from volume of moist gas is based on :
(a) Gay Lussac's law
(b) Dalton's law of partial pressures
(c) Boyle's law
(d) Avogadro's hypothesis.

A2. The pressure of a 1 : 4 mixture of dihydrogen and dioxygen enclosed in a vessel is one atmosphere. What would be the partial pressure of dioxygen?
(a) 0.8×10^5 atm
(b) 0.008 Nm^{-2}
(c) 8×10^4 Nm^{-2}
(d) 0.25 atm

A3. The temperature of a gas in a closed container is 27°C. If the temperature is raised to 327°C the pressure exerted is :
(a) reduced to half
(b) doubled
(c) reduced to one-third
(d) cannot be calculated from the given information.

A4. A gas at 10°C occupies a volume of 283 mL. If it is heated to 20°C keeping the pressure constant the new volume will be :
(a) 283 mL (b) 293 mL
(c) 566 mL (d) cannot be calculated from the given information.

A5. At constant temperature, the pressure of V mL of a dry gas was increased from 1 atm to 2 atm. The new volume will be :
(a) 2V (b) V/2
(c) V^2 (d) V/4.

A6. Equal masses of CH_4 and H_2 are mixed in an empty chamber. The partial pressure of hydrogen in this chamber expressed as fraction of total pressure is :
(a) 1/2 (b) 8/19
(c) 1/9 (d) 8/9.

A7. The density of a gas is 1.964 g dm^{-3} at 273 K and 76 cm Hg. The gas is
(a) Xe (b) CO_2
(c) C_2H_6 (d) CH_4

A8. The interaction energy of London force is inversely proportional to sixth power of the distance between two interacting particles but their magnitude depends upon
(a) charge of interacting particles
(b) mass of interacting particles
(c) polarisability of interacting particles
(d) strength of permanent dipoles in the particles

Answers

A1. (b) **A2.** (c) **A3.** (b) **A4.** (b) **A5.** (b) **A6.** (d) **A7.** (b) **A8.** (c)

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A9. For a given mass of a gas at constant temperature, if the volume V becomes three times, then the pressure (p) will become :
(a) $3p$ (b) $p/3$
(c) $3p/T$ (d) $9p^2$.

A10. An open vessel at 37°C is heated until 3/5 of the air in it has been expelled. Assuming that the volume of the vessel remains constant, the temperature to which the vessel is heated is :
(a) 502°C (b) 502 K
(c) 243.67°C (d) 92.5°C

A11. If air contains N_2 and O_2 in volume ratio 4 : 1, the average vapour density of air is :
(a) 14.4 (b) 15.5
(c) 16.5 (d) 29

A12. The gases H_2, N_2, O_2 and NH_3 will diffuse in the order :
(a) $H_2 > N_2 > O_2 > NH_3$ (b) $NH_3 > O_2 > N_2 > H_2$
(c) $H_2 > N_2 > NH_3 > O_2$ (d) $H_2 > NH_3 > N_2 > O_2$

A13. In what ratio by mass, sulphur trioxide and nitrogen should be mixed so that partial pressure exerted by each gas is same ?
(a) 7 : 20 (b) 7 : 40
(c) 20 : 7 (d) 40 : 7

A14. 20% N_2O_4 molecules are dissociated in a sample of gas at 27°C and 760 torr pressure. The density of equilibrium mixture is :
(a) 3.1 g L^{-1} (b) 6.2 g L^{-1}
(c) 12.4 g L^{-1} (d) 18.6 g L^{-1}.

A15. According to Graham's law, at given tempe-rature the ratio of the rates of diffusion r_A/r_B of gases A and B is given by :
(a) $(p_A/p_B)(M_A/M_B)^{1/2}$ (b) $(M_A/M_B)(p_A/p_B)^{1/2}$
(c) $(p_A/p_B)(M_B/M_A)^{1/2}$ (d) $(M_B/M_A)(p_A/p_B)^{1/2}$

A16. A person living in Shimla observed that cooking food without using pressure cooker takes more time. The reason for this observation is that at high altitude :
(a) pressure increases
(b) temperature decreases
(c) pressure decreases
(d) temperature increases

A17. On a humid day, the mole fraction of water vapour in air at 298K is 0.0265 bar. If total vapour pressure of air is 0.980 bar and vapour pressure of water at 298 K is 0.0315 bar, the relative humidity is
(a) 82.5 (b) 88.6
(c) 76.4 (d) 28.5

A18. The pyknometer density of NaCl crystal is 2.165×10^3 kg m^{-3} while its X-rays density is 2.178×10^3 kg m^{-3}. The fraction of the unoccupied sites in NaCl crystal is
(a) 5.96 (b) 5.96×10^{-2}
(c) 5.96×10^{-3} (d) 5.96×10^{-3}

A19. The rate of diffusion of methane is twice that of X. The molecular mass of X is
(a) 16 (b) 32
(c) 80 (d) 64

A20. Boyle's law expression may be expressed as :
(a) $\frac{dp}{p} = \frac{dV}{V}$ (b) $\frac{dp}{p} = -\frac{dV}{V}$
(c) $\frac{d^2p}{p} = -\frac{dV}{dT}$ (d) $\frac{dp}{p} = \frac{dV}{dT}$

Kinetic Molecular Theory of Gases

A21. The ratio of r.m.s. velocity and average velocity of a gas molecule at a particular temperature is :
(a) 1.086 : 1 (b) 1 : 1.086
(c) 2 : 1.086 (d) 1.086 : 2.

A22. The ratio of average speed of an oxygen molecule to the r.m.s. speed of a N_2 molecule at the same temperature is :
(a) $\left(\frac{3\pi}{7}\right)^{1/2}$ (b) $\left(\frac{7}{3\pi}\right)^{1/2}$
(c) $\left(\frac{3}{7\pi}\right)^{1/2}$ (d) $\left(\frac{7\pi}{3}\right)^{1/2}$

A23. Two samples of gases A and B are at the same temperature. The molecules of 'A' are travelling four times faster than molecules of 'B'. The ratio of M_A/M_B of their mass will be :
(a) 16 (b) 1/16
(c) 4 (d) 1/4

A24. The RMS velocity of CH_4 will become double its value at STP when the temperature is :
(a) 546 K (b) 819°C
(c) 546°C (d) 819 K

A25. The temperature at which hydrogen molecules have the same kinetic energy as oxygen molecules have at 40°C is :
(a) 40°C (b) 5°C
(c) 320°C (d) 640°C

A26. The molecular velocities of two gases at same temperature are v_1 and v_2 and their masses are m_1 and m_2 respectively. Which of the following expression is correct ?
(a) $\frac{m_1}{v_1^2} = \frac{m_2}{v_2^2}$ (b) $m_1v_1 = m_2v_2$
(c) $\frac{m_1}{v_1} = \frac{m_2}{v_2}$ (d) $m_1{v_1}^2 = m_2{v_2}^2$

Answers

A9. (b) **A10.** (a) **A11.** (a) **A12.** (d) **A13.** (c) **A14.** (a) **A15.** (c) **A16.** (c) **A17.** (a) **A18.** (d) **A19.** (d) **A20.** (b) **A21.** (a) **A22.** (b) **A23.** (b) **A24.** (b) **A25.** (a) **A26.** (d)

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A27. The r.m.s. velocity of hydrogen is $\sqrt{7}$ times the r.m.s. velocity of nitrogen. If T is temperature of the gas :

(a) $T(H_2) = T(N_2)$ (b) $T(H_2) > T(N_2)$

(c) $T(H_2) < T(N_2)$ (d) $T(H_2) = \sqrt{7}\ (N_2)$

A28. At what temperature will the total kinetic energy of 0.30 mol of helium be same as the total kinetic energy of 0.40 mol of argon at 500 K.

(a) 375 K (b) 666.7 K

(c) 573 K (d) 500 K

A29. As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by a factor of which of the following ?

(a) 313/293 (b) $\sqrt{313/293}$

(c) 1/2 (d) 2

A30. Which one of the following statement is not ture about the effect of an increase in temperature on the distribution of molecular speeds in a gas ?

(a) The most probable speed increases

(b) The fraction of molecules with the most probable speed increases

(c) The distribution becomes broder.

(d) The area under the distribution curve remains the same as under the lower temperature.

Ideal and Non-ideal Behaviour of Gases

A31. Real gases approach ideal behaviour at :

(a) low pressure and low temperature

(b) low pressure and high temperature

(c) high pressure and low temperature

(d) high pressure and high temperature.

A32. The van der Waals' equation accounts for :

(a) the intermolecular forces only

(b) the actual volume of the molecules only

(c) both the intermolecular forces and the molecular volume

(d) neither the intermolecular forces nor the molecular volume.

A33. In van der Waals equation for a non-ideal gas, the term which accounts for the intermolecular forces is :

(a) aV^2 (b) b

(c) RT (d) 1/RT.

A34. At extremely low pressure the Van der Waals equation of one mole may be written as :

(a) $pV = RT + pb$ (b) $(p + a)(V - b) = RT$

(c) $pV = RT - \frac{a}{V}$ (d) $pV = RT$

A35. The value of van der Waals constant 'a' for N_2 and NH_3 are 1.39 and 4.17 atm l^2 mol^{-2} respectively. If these two gases have the same value of constant 'b' then under similar conditions :

(a) The pressure exerted by N_2 gas is more than that of NH_3

(b) The pressure exerted by nitrogen is less than that of NH_3

(c) Both exert equal pressure

(d) None of these.

Liquid State

A36. Liquids diffuse slowly as compared to gases because

(a) liquids have no definite shape

(b) the molecules of liquid are heavy

(c) the molecules of liquid move fast

(d) the molecules are held together by strong intermolecular forces.

A37. On heating a liquid, its viscosity :

(a) increases (b) decreases

(c) remains same (d) is reduced to zero.

A38. At high altitudes, the boiling point of water gets lowered because :

(a) temperature is low

(b) atmospheric pressure is low

(c) atmospheric pressure is high

(d) none of these.

A39. The heats of vaporisation of H_2O, C_2H_5OH and CS_2 are 40.6, 38.6 and 26.8 kJ mol^{-1} respectively. The order of decreasing intermolecular forces in these liquids is :

(a) $H_2O > C_2H_5OH > CS_2$

(b) $CS_2 > C_2H_5OH > H_2O$

(c) $H_2O > CS_2 > C_2H_5OH$

(d) $CS_2 > H_2O > C_2H_5OH$

A40. Which of the following property of water be used to explain the spherical shape of rain droplets?

(a) viscosity (b) surface tension

(c) critical phenomena (d) pressure

A41. The surface tension of which of the following liquid is maximum ?

(a) C_2H_5OH (b) CH_3OH

(c) H_2O (d) C_6H_6

Answers

A27. (c) **A28.** (b) **A29.** (a) **A30.** (b) **A31.** (b) **A32.** (c) **A33.** (a) **A34.** (c) **A35.** (a) **A36.** (d) **A37.** (b) **A38.** (b) **A39.** (a) **A40.** (b) **A41.** (c)

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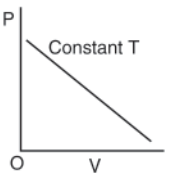
B MULTIPLE CHOICE QUESTIONS *from competitive examinations*

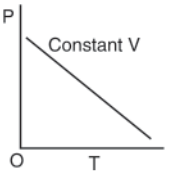
AIPMT & Other State Boards' Medical Entrance

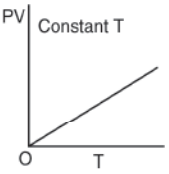
B1. If the ratio of the masses of SO_3 and O_2 gases confined in a vessel is 1:1, then the ratio of their partial pressures would be

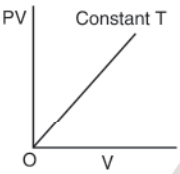
(*a*) 5 : 2 (*b*) 2 : 5
(*c*) 2 : 1 (*d*) 1 : 2
(*e*) 1 : 1 *(Kerala P.M.T. 2007)*

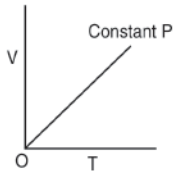
B2. Which of the following diagram correctly describes the behaviour of a fixed mass of an ideal gas ? (T is measured in K).

(*a*) 

(*b*) 

(*c*) 

(*d*) 

(*e*) 

(Kerala P.M.T. 2007)

B3. When a bottle of dry ammonia and a bottle of dry HCl connected through a long tube are opened simultaneously at both ends, at first

(*a*) a white ring is formed at the centre of the tube
(*b*) a white ring is formed near the ammonia bottle
(*c*) entire length of tube turns white
(*d*) a white ring is formed near HCl bottle
(*e*) no white ring is formed *(Kerala P.M.T. 2008)*

B4. A 4.0 dm^3 flask containing N_2 at 4.0 bar was connected to a 6.0 dm^3 flask containing helium at 6.0 bar and the gases were allowed to mix isothermally. Then the total pressure of the resulting mixture will be

(*a*) 10.0 bar (*b*) 5.2 bar
(*c*) 3.6 bar (*d*) 1.6 bar
(e) 5.0 bar *(Kerala P.M.T. 2008)*

B5. If a gas expands at constant temperature, it indicates that

(*a*) kinetic energy of molecules decreases
(*b*) pressure of gas increases
(*c*) kinetic energy of molecules remains the same
(*d*) number of molecules of gas increases.
(C.B.S.E. P.M.T. 2008)

B6. Critical temperatures of H_2O, NH_3, CO_2 and O_2 are 647 K, 405.6 K, 304.10 K and 154.2 K respectively. If the cooling starts from 500 K to their critical temperature, the gas that liquefies first is

(*a*) H_2O (*b*) NH_3
(*c*) CO_2 (*d*) O_2 *(A.M.U.-Med. 2009)*

B7. What will happen to the volume of a bubble of air found under water in a lake, where the temperature is 15°C and the pressure is 1.5 atm, if the bubble then rises to the surface where the temperatue is 25°C and the pressure is 1.0 atm ?

(*a*) Its volume will become greater by a factor of 2.5
(*b*) Its volume will become greater by a factor of 1.6
(*c*) Its volume will become greater by a factor of 1.1
(*d*) Its volume will become greater by a factor of 0.70
(DUMET 2010)

B8. The incorrect statement among the following is

(*a*) The boiling point of a liquid at one bar is called standard boiling point of the liquid.
(*b*) The vapour pressure of a liquid is constant at constant temperature.
(*c*) The SI unit of coefficient of viscosity of a liquid is pascal second.
(*d*) The surface tension of a liquid decreases with increase of temperature.
(*e*) The boiling point of a liquid is the same at all external pressure. *(Kerala PMT 2010)*

B9. An evacuated glass vessel weighs 50 g when empty, 144.0 g when filled with a liquid of density 0.47 g mL^{-1} and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. The molar mass of the ideal gas is (Given R = 0.0821 L atm K^{-1} mol^{-1})

(*a*) 61.575 (*b*) 130.98
(*c*) 123.75 (*d*) 43.87
(*e*) 87.943 *(Kerala PMT 2010)*

B10. The mass of 2.24×10^{-3} m^3 of a gas is 4.4 g at 273.15 K and 101.325 kPa pressure. The gas may be

(*a*) NO (*b*) NO_2
(*c*) C_3H_8 (*d*) NH_3
(*e*) CH_4 *(Kerala PMT 2010)*

B11. A bubble of gas released at the bottom of a lake increases to eight times its original volume when it reaches the surface. Assuming that atmospheric pressure is equivalent to the pressure exerted by a column of water 10 m height, the depth of the lake is

(*a*) 80 m (*b*) 90 m
(*c*) 40 m (*d*) 10 m
(*e*) 70 m *(Kerala PMT 2011)*

Answers

B1. (*b*) **B2.** (*e*) **B3.** (*d*) **B4.** (*b*) **B5.** (*c*) **B6.** (*a*) **B7.** (*b*) **B8.** (*e*) **B9.** (*a*) **B10.** (*c*) **B11.** (*e*)

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B12. A gaseous mixture was prepared by taking equal mole of CO and N_2. If the total pressure of the mixture was found 1 atmosphere, the partial pressure of the nitrogen (N_2) in the mixture is

(*a*) 0.5 atm (*b*) 0.8 atm
(*c*) 0.9 atm (*d*) 1 atm *(AIPMT 2011)*

B13. Two gases A and B having the same volume diffuse through a porous partition in 20 and 10 seconds respectively. The molecular mass of A is 49u. Molecular mass of B will be

(*a*) 50.0 u (*b*) 12.25 u
(*c*) 6.50 u (*d*) 25.0 u *(AIPMT 2011)*

B14. By what factor does the average velocity of a gaseous molecule increases when the temperature (in Kelvin) is doubled.

(*a*) 2.0 (*b*) 2.8
(*c*) 4.0 (*d*) 1.4 *(AIPMT 2011)*

B15. A mixture contains 64 g of dioxygen and 60 g of neon at a total pressure of 10 bar. The partial pressures in bar of dioxygen and neon are respectively (atomic masses : O = 16, Ne = 20)

(*a*) 4 and 6 (*b*) 6 and 4
(*c*) 5 and 5 (*d*) 8 and 2
(*e*) 2 and 8 *(Kerala P.M.T. 2012)*

B16. Choose the incorrect statement in the following:

(*a*) Surface tension is the force acting per unit length perpendicular to the line drawn on the surface of the liquid.
(*b*) Surface tension of a liquid increases with increase in temperature.
(*c*) The SI unit of surface tension is Jm^{-2}
(*d*) Viscosity is a measure of resistance for the flow of liquid.
(*e*) Viscosity of a liquid decreases with increase of temperature. *(Kerala P.M.T. 2012)*

B17. The gas with the highest critical temperature is

(*a*) H_2 (*b*) He
(*c*) N_2 (*d*) O_2
(*e*) CO_2 *(Kerala P.M.T. 2012)*

B18. 50 mL of each gas A and of gas B takes 150 and 200 seconds respectively for effusing through a pin hole under the similar conditions. If molecular mass of gas A is 36, the molecular mass of gas B will be

(*a*) 96 (*b*) 128
(*c*) 32 (*d*) 64 *(A.I.P.M.T. 2012)*

B19. The compressibility factor for a real gas at high pressure is

(*a*) 1 (*b*) 1 + pb/RT
(*c*) 1 – pb/RT (*d*) 1 + RT/pb
(A.I.P.M.T. 2012)

B20. The average energy per molecule of a gas at a given temperature, T, is given by

(*a*) $\frac{3}{2}RT$ (*b*) $\sqrt{\frac{3RT}{M}}$
(*c*) $\sqrt{\frac{8\left(R/N_A\right)T}{\pi M}}$ (*d*) $\frac{3}{2}\left(\frac{R}{N_A}\right)T$
(A.M.U. Med. 2013)

B21. When 4 g of an ideal gas A is introduced into an evacuated flask kept at 25°C, the pressure is found to be one atmosphere. If 6 g of another ideal gas B is then added to the same flask, the pressure becomes 2 atm at same temperature. The ratio of molecular weights ($M_A : M_B$) of the two gases would be

(*a*) 1 : 2 (*b*) 2 : 1
(*c*) 2 : 3 (*d*) 3 : 2
(*e*) 1 : 4 *(Kerala P.M.T. 2013)*

B22. The volume of neon gas in cm^3 at STP having the same number of atoms as that present in 800 mg of Ca is (At. mass : Ca = 40 g mol^{-1}, Ne = 20 g mol^{-1})

(*a*) 56 (*b*) 896
(*c*) 224 (*d*) 112
(*e*) 448 *(Kerala P.M.T. 2013)*

B23. Which of the following is not the postulate of the kinetic theory of gases?

(*a*) Gas molecules are in a permanent state of random motion.
(*b*) Pressure of gas is due to molecular impacts on the walls
(*c*) The molecules are perfectly elastic
(*d*) The molecular collisions are elastic.
(Kerala P.M.T. 2013)

B24. Maximum deviation from ideal gas is expected from

(*a*) $CH_4(g)$ (*b*) $NH_3(g)$
(*c*) $H_2(g)$ (*d*) $N_2(g)$ *(NEET 2013)*

B25. Dipole-induced dipole interactions are present in which of the following pairs?

(*a*) HCl and He atoms (*b*) SiF_4 and He atoms
(*c*) H_2O and alcohol (*d*) Cl_2 and CCl_4
(NEET 2013)

Answers

B12. *(a)* **B13.** *(b)* **B14.** *(d)* **B15.** *(a)* **B16.** *(b)* **B17.** *(e)* **B18.** *(d)* **B19.** *(b)* **B20.** *(d)* **B21.** *(c)*
B22. *(e)* **B23.** *(c)* **B24.** *(b)* **B25.** *(a)*

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B26. Equal masses of H_2, O_2 and methane have been taken in a container of volume V at temperature 27°C in identical conditions. The ratio of the volumes of gases H_2 : O_2 : methane would be
(*a*) 8 : 16 : 1 (*b*) 16 : 8 : 1
(*c*) 16 : 1 : 2 (*d*) 8 : 1 : 2 *(AIPMT 2014)*

B27. Equal masses of He, O_2 and SO_2 are taken in a closed container. The ratio of the partial pressures of gases He, O_2 and SO_2 would be
(*a*) 1 : 2 : 8 (*b*) 8 : 16 : 1
(*c*) 16 : 8 : 1 (*d*) 1 : 4 : 16
(*e*) 16 : 2 : 1 *(Kerala PMT 2015)*

B28. Which one of the following gases has the highest critical temperature?
(*a*) Nitrogen (*b*) Ammonia
(*c*) Water vapour (*d*) Carbon dioxide
(*e*) Hydrogen *(Kerala PMT 2015)*

B29. A gas such as carbon monoxide would be most likely to obey the ideal gas law at:
(*a*) high temperatures and high pressures.
(*b*) low temperatures and low pressures.
(*c*) high temperatures and low pressures.
(*d*) low temperatures and high pressures.
(AIPMT 2015)

B30. Equal moles of hydrogen and oxygen gases are placed in a container with a pin–hole through which both can escape. What fraction of the oxygen escapes in the time required for one–half of the hydrogen to escape?
(*a*) 3/8 (*b*) 1/2
(*c*) 1/8 (*d*) 1/4 *(NEET 2016)*

B31. Given van der Waals' constant for NH_3, H_2, O_2 and CO_2 are respectively 4.17, 0.244, 1.36, and 3.59, which one of the following gases is most easily liquefied?
(*a*) NH_3 (*b*) H_2
(*c*) O_2 (*d*) CO_2 *(NEET 2018)*

B32. The correction factor '*a*' to the ideal gas equation corresponds to
(*a*) density of the gas molecules
(*b*) volume of the gas molecules
(*c*) electric field present between the gas molecules
(*d*) forces of attraction between the gas molecules
(NEET 2018)

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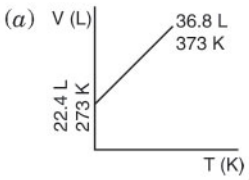
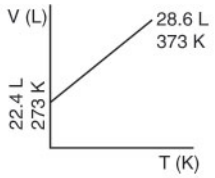
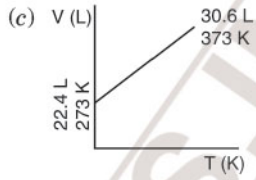
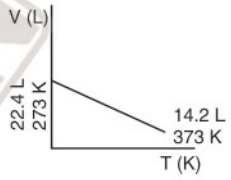
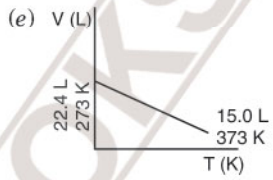
B33. Which one of the following volume (V) – temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmosphere ?

(*a*) 

(*b*) 

(*c*) 

(*d*) 

(*e*) 

(Kerala C.E.T. 2007)

B34. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of total pressure exerted by oxygen is
(*a*) $\frac{1}{3} \times \frac{273}{298}$ (*b*) $\frac{1}{3}$
(*c*) $\frac{1}{2}$ (*d*) $\frac{2}{3}$ *(A.I.E.E.E. 2007)*

B35. In order to increase the volume of a gas by 10%, the pressure of the gas should be
(*a*) decreased by 10%
(*b*) decreased by 1%
(*c*) increased by 10%
(*d*) increased by 1% *(Karnataka C.E.T. 2008)*

B36. 100 mL of O_2 and H_2 are kept at same temperature and pressure. What is true about their number of molecules ?
(*a*) $N_{O_2} > N_{H_2}$ (*b*) $N_{O_2} < N_{H_2}$
(*c*) $N_{O_2} = N_{H_2}$ (*d*) $N_{O_2} + N_{H_2} = 1$ mole
(Orissa JEE 2009)

B37. The r.m.s. velocity of molecules of a gas of density 4 kg/m^3 and pressure 1.2×10^5 N/m^2 is
(*a*) 900 m/s (*b*) 120 m/s
(*c*) 600 m/s (*d*) 300 m/s
(Karnataka C.E.T. 2009)

B38. At what temperature, will the rms velocity of a gas at 50°C be doubled?
(*a*) 626 K (*b*) 1019 K
(*c*) 200°C (*d*) 1019°C
(Orissa JEE 2010)

Answers

B26. *(c)* **B27.** *(e)* **B28.** *(c)* **B29.** *(c)* **B30.** *(c)* **B31.** *(a)* **B32.** *(d)* **B33.** *(c)* **B34.** *(b)* **B35.** *(a)* **B36.** *(c)* **B37.** *(d)* **B38.** *(d)*

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B39. The density of gas A is twice that of B. Molecular mass of A is half of molecular mass of B. The ratio of partial pressure of A and B is

(a) $\frac{1}{4}$ (b) $\frac{1}{2}$

(c) $\frac{4}{1}$ (d) $\frac{2}{1}$ *(Orissa JEE 2010)*

B40. At identical temperature and pressure, the rate of diffusion of hydrogen gas is $3\sqrt{3}$ times that of a hydrocarbon having molecular formula C_nH_{2n-2}. What is the value of n?

(a) 1 (b) 4

(c) 3 (d) 8 *(West Bengal JEE 2010)*

B41. For one mole of an ideal gas, increasing the temperature from 10°C to 20°C

(a) increases the average kinetic energy by two times

(b) increases the rms velocity by $\sqrt{2}$ times

(c) increases the rms velocity by two times

(d) increases both the average kinetic energy and rms velocity, but not significantly *(Karnataka CET 2010)*

B42. If 10^{-4} dm^3 of water is introduced into a 1.0 dm^3 flask at 300 K, how many moles of water are in the vapour phase when equilibrium is established?
(Given : Vapour pressure of H_2O at 300 K is 3170 Pa ; R = 8.314 J K^{-1} mol^{-1})

(a) 4.46×10^{-2} mol (b) 1.27×10^{-3} mol

(c) 5.56×10^{-3} mo (d) 1.53×10^{2} mol *(AIEEE 2010)*

B43. Chemically unreactive three different gases A, B and C of molecular masses 16, 32 and 64 are enclosed in a vessel at constant temperature till equilibrium is reached. Which of the following statement is true ?

(a) Gas A will be at the top of the vessel.

(b) Gas C will be at the top of the vessel.

(c) Gas C will be at the bottom of the vessel.

(d) Gases will form homogeneous mixture. *(J.K. CET 2011)*

B44. The rms velocity of hydrogen is $\sqrt{7}$ times the rms velocity of nitrogen. If T is the temperature of the gas, which of the following is true ?

(a) $T_{N_2} = T_{H_2}$ (b) $T_{H_2} = \sqrt{7}\ T_{N_2}$

(c) $T_{N_2} = 2\ T_{H_2}$ (d) $T_{N_2} = \sqrt{7}\ T_{H_2}$ *(Karnataka CET 2011)*

B45. 'a' and 'b' are van der Waals constants for gases. Chlorine is more easily liquefied than ethane because

(a) a and b for $Cl_2 > a$ and b for C_2H_6

(b) a and b for $Cl_2 < a$ and b for C_2H_6

(c) a for $Cl_2 < a$ for C_2H_6 but b for $Cl_2 > b$ for C_2H_6

(d) a for $Cl_2 > a$ for C_2H_6 but b for $Cl_2 < b$ for C_2H_6 *(AIEEE 2011)*

B46. Two vessels of volumes 16.4 L and 5 L contain two ideal gases of molecular existence at the respective temperature of 27°C and 227°C and exert 1.5 and 4.1 atmospheres respectively. The ratio of the number of molecules of the former to that of the latter is

(a) 2 (b) 1

(c) $\frac{1}{2}$ (d) $\frac{1}{3}$

(e) 3 *(Kerala P.E.T. 2013)*

B47. For gaseous state, if most probable speed is denoted by C*, average speed by $\bar{C}$ and mean square speed by C, then for a larger number of molecules the ratios of these speed are

(a) C* : $\bar{C}$: C = 1 : 1.225 : 1.128

(b) C* : $\bar{C}$: C = 1.225 : 1.128 : 1

(c) C* : $\bar{C}$: C = 1.128 : 1 : 1.225

(d) C* : $\bar{C}$: C = 1 : 1.128 : 1.225 *(JEE Main 2013)*

B48. For one mole of an ideal gas, the slope of V vs T curve at constant pressure of 2 atm is X L mol^{-1} K^{-1}. The value of the ideal universal gas constant 'R' in terms of X is

(a) X L atm mol^{-1} K^{-1} (b) X/2 L atm mol^{-1} K^{-1}

(c) 2X L atm mol^{-1} K^{-1} (d) 2X atm L^{-1} mol^{-1} K^{-1} *(WB JEE 2014)*

B49. At a certain temperature, the time required for the complete diffusion of 200 mL of H_2 gas is 30 minutes. The time required for the complete diffusion of 50 mL of O_2 gas at the same temperature will be

(a) 60 minutes (b) 30 minutes

(c) 45 minutes (d) 15 minutes *(WB JEE 2014)*

B50. Four gases P, Q, R and S have almost same values of 'b' but their 'a' values (a, b are van der Waals constants) are in the order Q < R < S < P. At a particular temperature, among the four gases the most easily liquefiable one is

(a) P (b) Q

(c) R (d) S *(WB JEE 2014)*

B51. If two moles of an ideal gas at 500 K occupies a volume of 41 litres, the pressure of the gas is
(R = 0.082 L atm K^{-1} mol^{-1})

(a) 2 atm (b) 3 atm

(c) 4 atm (d) 5 atm

(e) 1 atm *(Kerala PET 2014)*

Answers

B39. *(c)* **B40.** *(b)* **B41.** *(d)* **B42.** *(b)* **B43.** *(d)* **B44.** *(c)* **B45.** *(d)* **B46.** *(a)* **B47.** *(d)* **B48.** *(c)* **B49.** *(b)* **B50.** *(a)* **B51.** *(a)*

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B52. At 273 K, the density of a certain gaseous oxide at 2 atmosphere is same as that of dioxygen at 5 atmosphere. The molecular mass of the oxide (in g mol^{-1}) is
(*a*) 80 (*b*) 64
(*c*) 32 (*d*) 160
(*e*) 70 (*Kerala PET 2014*)

B53. Density of carbon monoxide is maximum at
(*a*) 2 atm and 600 K (*b*) 0.5 atm and 273 K
(*c*) 6 atm and 1092 K (*d*) 4 atm and 500 K
(*Karnataka CET 2014*)

B54. If Z is a compressibility factor, van der Waals equation at low pressure can be written as
(*a*) $Z = 1 + \frac{pb}{RT}$ (*b*) $Z = 1 + \frac{RT}{pb}$
(*c*) $Z = 1 - \frac{a}{VRT}$ (*d*) $Z = 1 - \frac{pb}{RT}$
(*JEE Main 2014*)

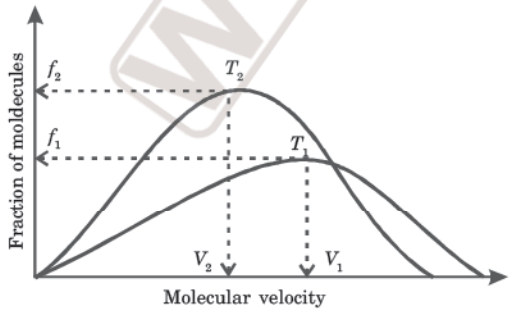
B55. One mole of N_2O_4 (*g*) at 300 K is kept in a closed vessel at 1 atm pressure. It is heated to 600 K when 20% by mass of N_2O_4 (*g*) decomposes to NO_2 (*g*). The resultant pressure is
(*a*) 1.2 atm (*b*) 2.4 atm
(*c*) 2.0 atm (*d*) 1.0 atm
(*AMU Engg. 2015*)

B56. The units of surface tension and viscosity of liquids are respectively
(*a*) kg $m^{-1}s^{-1}$, Nm^{-1} (*b*) kg s^{-2},kg m^{-1} s^{-1}
(*c*) N m^{-1},kg m^{-1} s^{-2} (*d*) kg s^{-1},kg m^{-2} s^{-1}
(*WB JEE. 2015*)

B57. A gas can be liquefied at temperature T and pressure P provided
(*a*) $T = T_c$ and $P < P_c$ (*b*) $T < T_c$ and $P > P_c$
(*c*) $T > T_c$ and $P > P_c$ (*d*) $T > T_c$ and $P < P_c$
(*WB JEE. 2015*)

B58. The rms velocity of CO gas molecules at 27°C is approximately 1000 m/s. For N_2 molecules at 600 K the rms velocity is approximately
(*a*) 2000 m/s (*b*) 1414 m/s
(*c*) 1000 m/s (*d*) 1500 m/s
(*WB JEE. 2015*)

B59. Plot of Maxwell's distribution of velocities is given below:



Which of the following is correct about this plot?
(*a*) $f_1 > f_2$ (*b*) $V_1 < V_2$
(*c*) $T_1 < T_2$ (*d*) $T_1 > T_2$
(*Karnataka CET 2015*)

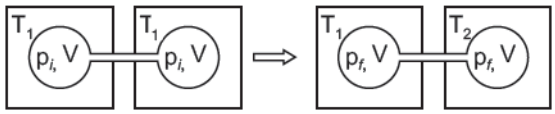
B60. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is
(*a*) London force
(*b*) hydrogen bond
(*c*) ion-ion interaction
(*d*) ion-dipole interaction. (*JEE Main 2015*)

B61. Dipole–dipole interaction energy between polar molecules in solids depends on the radius of the molecule (*r*) and it is directly proportional to
(*a*) $(1/r^2)$ (*b*) $(1/r^6)$
(*c*) $(1/r)$ (*d*) $(1/r^5)$
(*e*) $(1/r^3)$ (*Kerala PET 2016*)

B62. Critical density of a gas having molecular weight 39 *g* mol^{-1} is 0.1 *g* cm^{-3}. Its critical volume in *L* mol^{-1} is
(*a*) 0.390 (*b*) 3.90
(*c*) 0.039 (*d*) 39.0
(*e*) 390 (*Kerala PET 2016*)

B63. A liquid can exist only
(*a*) between triple point and critical point
(*b*) at any temperature above melting point
(*c*) between melting point and critical point
(*d*) between boiling and melting points.
(*Karnataka C.E.T 2016*)

B64. Two closed bulbs of equal volume (V) containing an ideal gas intially at pressure p_i and temperature T_1 are connnected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to T_2. The final pressure p_f is



(*a*) $p_i\left(\frac{T_1T_2}{T_1+T_2}\right)$
(*b*) $2p_i\left(\frac{T_1}{T_1+T_2}\right)$
(*c*) $2p_i\left(\frac{T_2}{T_1+T_2}\right)$
(*d*) $2p_i\left(\frac{T_1T_2}{T_1+T_2}\right)$
(*JEE Main 2016*)

Answers

B52. (*a*) **B53.** (*d*) **B54.** (*c*) **B55.** (*b*) **B56.** (*b*) **B57.** (*b*) **B58.** (*b*) **B59.** (*d*) **B60.** (*b*) **B61.** (*e*) **B62.** (*a*) **B63.** (*d*) **B64.** (*c*)

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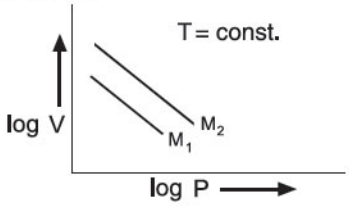
B65. For same mass of two different ideal gases of molecular weights M_1 and M_2, plots of log V vs log P at a given constant temperature are shown. Identify the correct option.



(a) $M_1 > M_2$
(b) $M_1 = M_2$
(c) $M_1 < M_2$
(d) Can be predicted only if temperature is known

(WB JEE 2017)

B66. Which of the following has the dimension of ML^0T^{-2}?
(a) Coefficient of viscosity
(b) Surface tension
(c) Vapour pressure
(d) Kinetic energy

(WB JEE 2017)

B67. The pressure of real gas is less than that of ideal gas because of
(a) increase in the kinetic energy of the molecules
(b) intermolecular attraction
(c) finite size of particles
(d) increase in the number of collisions.

(Karnataka CET 2017)

B68. A gas will approach ideal behaviour at
(a) low temperature and low pressure
(b) low temperature and high pressure
(c) high temperature and low pressure
(d) high temperature and high pressure
(e) low volume and high pressure.

(Kerala PET 2017)

B69. Pressure of ideal and real gases at 0 K are
(a) > 0 and 0 (b) < 0 and 0
(c) 0 and 0 (d) > 0 and > 0
(e) 0 and > 0

(Kerala PET 2017)

B70. What will be the relation between T_1 of gas 1 with M_1 = 56 and T_2 of gas 2 with M_2 = 44 if the average speed of gas 1 is equal to most probable speed of gas 2?
(a) $T_1 = T_2^2$ (b) $T_1 = T_2$
(c) $T_1 = (T_2)^{1/2}$ (d) $T_1 = 1/T_2$

(J.K. CET 2018)

B71. Which equation will explain the nature of PV versus P curve for CO_2 gas at moderately low pressure?
(a) $PV = RT + Pb$ (b) $PV = RT + a/V$
(c) $PV = RT - a/V$ (d) $PV = RT - aV$

(J.K. CET 2018)

B72. For an ideal gas, compressibility factor is
(a) 0 (b) 1
(c) –1 (d) +2

(Karnataka CET 2018)

B73. Equal weights of ethane and hydrogen are mixed in an empty container at 25 °C. The fraction of total pressure exerted by hydrogen is
(a) 1 : 2 (b) 1 : 1
(c) 1 : 16 (d) 15 : 16

(WB JEE 2018)

B74. A compound of formula A_2B_3 has the hcp lattice. Which atom forms the hcp lattice and what fraction of tetrahedral voids is occupied by the other atoms:
(a) hcp lattice-A, $\frac{2}{3}$ tetrahedral voids-B
(b) hcp lattice-B, $\frac{1}{3}$ tetrahedral voids-A
(c) hcp lattice-B, $\frac{2}{3}$ tetrahedral voids-A
(d) hcp lattice-A, $\frac{1}{3}$ tetrahedral voids-B

(JEE Main 2019)

B75. The volume of gas A is twice than that of gas B. The compressibility factor of gas A is thrice than that of gas B at same temperature. The pressure of the gases for equal number of moles are
(a) $P_A = 2P_B$ (b) $P_A = 3P_B$
(c) $3P_A = 2P_B$ (d) $2P_A = 3P_B$

(JEE Main 2019)

JEE (Advance) for IIT Entrance

B76. The compressibility of a gas is less than unity at S.T.P. Therefore,
(a) $V_m > 22.4$ litres (b) $V_m < 22.4$ litres
(c) $V_m = 22.4$ litres (d) $V_m > 44.8$ litres

(I.I.T. Screening 2000)

B77. The root mean square velocity of an ideal gas at constant pressure varies with density (d) as :
(a) d^2 (b) d
(c) $\sqrt{d}$ (d) $\frac{1}{\sqrt{d}}$

(I.I.T. Screening 2001)

B78. When the temperature is increased, surface tension of water.
(a) increases
(b) decreases
(c) remains constant
(d) shows irregular behaviour

(I.I.T. Screening 2002)

Answers

B65. (a) **B66.** (b) **B67.** (b) **B68.** (c) **B69.** (c) **B70.** (b) **B71.** (c) **B72.** (b) **B73.** (d) **B74.** (b) **B75.** (a) **B76.** (b) **B77.** (d) **B78.** (b)

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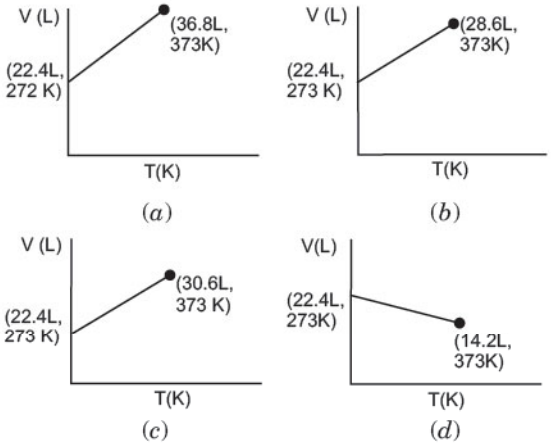
B79. Which of the following volume (V) – temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmopshere ?



(I.I.T. Screening 2002)

B80. Positive deviation from ideal gas behaviour takes placess because of

(*a*) molecular interaction between atoms and $pV/nRT > 1$

(*b*) molecular interactions between atoms and $pV/nRT < 1$

(*c*) finite size of the atoms and $pV/nRT > 1$

(*d*) fintie size of the atoms and $pV/nRT < 1$

(I.I.T. Screening 2003)

B81. The root mean square velocity of one mole of a monoatomic gas having molar mass M is $u_{r.m.s}$. The relation between the average kinetic energy (E) of the gas and $u_{r.m.s}$ is

(*a*) $u_{r.m.s} = \sqrt{\frac{3E}{2M}}$ (*b*) $u_{r.m.s} = \sqrt{\frac{2E}{3M}}$

(*c*) $u_{r.m.s} = \sqrt{\frac{2E}{M}}$ (*d*) $u_{r.m.s} = \sqrt{\frac{E}{3M}}$

(I.I.T. Screening 2004)

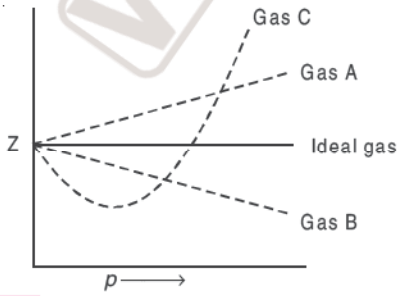
B82. The ratio of the rate of diffusion of helium and methane under identical conditions of temperature and pressure will be

(*a*) 4 (*b*) 2

(*c*) 1 (*d*) 0.5

(I.I.T. Screening 2005)

B83. Consider the following plot :



Which of the following statement is wrong ?

(*a*) For a gas A, $a = 0$, and Z will linearly depend on pressure.

(*b*) For gas B, $b = 0$, and Z will linearly depend on pressure.

(*c*) Gas C is a real gas and we can find 'a' and 'b' if intersection data is given.

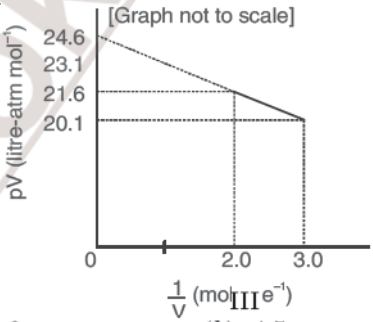
(*d*) All van der Waals gases will behave like gas C and gives positive slope at high pressure. *(I.I.T. 2006)*

B84. The term that corrects for the attractive forces present in a real gas in the van der Waals' equation is

(*a*) nb (*b*) $\frac{an^2}{V^2}$

(*c*) $-\frac{an^2}{V^2}$ (*d*) $-nb$ *(IIT 2009)*

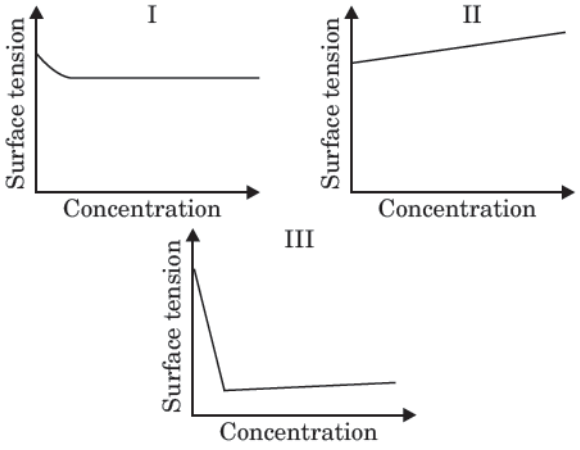
B85. For one mole of a van der Waals' gas, when $b = 0$ and $T = 300$ K, the pV vs 1/V plot is shown below. The value of the van der Waals' constant a atm litre^{-2} mol^{-2} is



(*a*) 1.0 (*b*) 4.5

(*c*) 1.5 (*d*) 3.0 *(I.I.T. J.E.E. 2012)*

B86. The qualitative sketches I, II, and III given below show the variation of surface tension with molar cocentration of three different aqueous solutions KCl, CH_3OH and $CH_3(CH_2)_{11}OSO_3^-Na^+$ at room temperature. The correct assignment of the sketches is



(*a*) I : KCl II : CH_3OH III : $CH_3(CH_2)_{11}OSO_3^-Na^+$

(*b*) I : $CH_3(CH_2)_{11}OSO_3^-Na^+$ II : CH_3OH III : KCl

(*c*) I : KCl II : $CH_3(CH_2)_{11}OSO_3^-Na^+$ III : CH_3OH

(*d*) I : CH_3OH II : KCl III : $CH_3(CH_2)_{11}OSO_3^-Na^+$

(JEE Advance 2016)

Answers

B79. *(c)* **B80.** *(a)* **B81.** *(c)* **B82.** *(b)* **B83.** *(b)* **B84.** *(b)* **B85.** *(c)* **B86.** *(d)*

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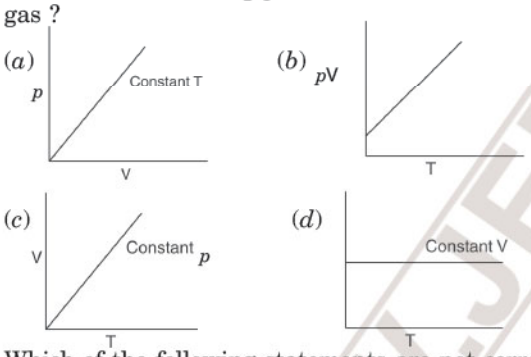
C MULTIPLE CHOICE QUESTIONS
with more than one correct answer

C1. Which of the following statements is /are correct?
(*a*) At constant temperature, the gas density is directly proportional to pressure.
(*b*) At higher pressures, gases deviate from Boyle's law.
(*c*) Plots of *p* vs T at constant volumes for an ideal gas are parabolic.
(*d*) At –273 K gases have zero volume which corresponds to solid state.

C2. Which of the following postulates of kinetic theory of gases are not correct ?
(*a*) Every gas is made up of a large number of extremely small particles.
(*b*) The distance of separation between these particles are very small.
(*c*) The force of gravitation on the particles is strong enough to keep the particles in constant motion.
(*d*) During motion, the particles collide with one another as well as on the walls of the container.

C3. Which of the following plots are correct for an ideal gas ?



C4. Which of the following statements are not correct ?
(*a*) Surface tension of liquids decreases with increase of temperature.
(*b*) The viscosity of a liquid increases with decrease of temperature.
(*c*) Liquids diffuse faster than gases.
(*d*) Gases can be liquefied only above their critical temperatures.

C5. Which of the following relations are not correct for van der Waals' equation for one mole of a gas ?
(*a*) At very low pressure, van der Waals' equation becomes pV = RT.
(*b*) At high pressure, compresibility is greater than one.
(*c*) At moderate pressures, compresibility is greater than one.
(*d*) Units of van der Waals' constant '*a*' are atm $L^2\ mol^{-2}$.

C6. A gas described by van der Waals' equation
(*a*) behaves similar to an ideal gas in the limit of large molar volumes
(*b*) behaves similar to an ideal gas in the limit of large pressures
(*c*) is characterised by van der Waals' coefficients that are dependent directly on identity of gas but are independent of temperature
(*d*) has the pressure that is lower than the pressure exerted by the same behaving ideally.
(I.I.T. 2008)

C7. Which of the following changes decrease the vapour pressure of water kept in a sealed vessel?
(*a*) Decreasing the quantity of water
(*b*) Adding salt to water
(*c*) Decreasing the volume of the vessel to one-half
(*d*) Decreasing the temperature of water

C8. Under which of the following two conditions applied together, a gas deviates most from the ideal behaviour?
(*a*) Low pressure (*b*) High pressure
(*c*) Low temperature (*d*) High temperature

C9. According to kinetic theory of gases
(*a*) collisions are always elastic
(*b*) heavier molecules transfer more momentum to the walls of the container
(*c*) only a small number of molecules have very high velocity
(*d*) between collisions, the molecules move in straight lines with constant velocities.
(I.I.T. 2011)

C10. Two gases X (mol. wt. M_X) and Y (mol. wt. M_Y ; $M_Y > M_X$) are at the same temperature T in two different containers. Their root mean square velocities are C_X and C_Y respectively. If the average kinetic energies per molecule of two gases X and Y are E_X and E_Y respectively, then which of the following relation (s) is (are) true ?
(*a*) $E_X > E_Y$ (*b*) $C_X > C_Y$
(*c*) $E_X = E_Y = \frac{3}{2}RT$ (*d*) $E_X = E_Y = \frac{3}{2}k_BT$
(WB JEE 2014)

Answers

C1. *(a,b)* **C2.** *(b,c)* **C3.** *(a,c)* **C4.** *(c,d)* **C5.** *(b,c)* **C6.** *(a,c,d)* **C7.** *(b,d)* **C8.** *(b, c)* **C9.** *(a, b, d)* **C10.** *(b, d)*

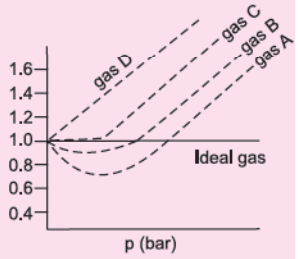
D MULTIPLE CHOICE QUESTIONS
based on the given passage/comprehension

Passage I.

The real gases show deviations from ideal behaviour. It is observed that real gases donot follow Boyle's law, Charles law and Avogadro law perfectly under all conditions. The deviations from ideal behaviour can be measured in terms of compressibility factor, Z, which may be defined as :

$$Z = \frac{pV}{nRT}$$

It has been observed that Z has values greater than and less than one for different gases. The behaviour of some common gases is shown here:



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Answer the following questions:

D1. For ideal gas, the compressibility factor is
(*a*) 1 (*b*) 0 (*c*) infinite (*d*) very very small

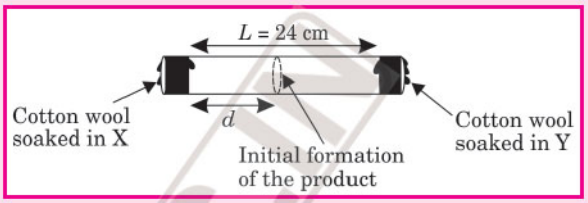
D2. The gas which is more compressible at low pressure and less compressible at high pressures than expected from ideal behaviour is /are
(*a*) A (*b*) B (*c*) D (*d*) both A and B

D3. The gas which is less compressible than expected from ideal behaviour is /are
(*a*) A (*b*) C (*c*) D (*d*) both B and C

D4. If V_o is the observed volume of a gas and V_i is the ideal gas volume, then Z is
(*a*) $V_o - V_i$ (*b*) V_o / V_i
(*c*) V_i / V_o (*d*) $V_i - V_o$

D5. For one mole of gas D, the van der Waals equation reduces to the form :
(*a*) $pV = RT - \frac{a}{V}$ (*b*) $pV = RT$
(*c*) $pV = RT + pb$ (*d*) $pV = RT - pb$

Passage II.
X and Y are two volatile liquids with molar weights of 10 g mol^{-1} and 40 g mol^{-1} respectively. Two cotton plugs, one soaked in X and the other soaked in Y, are simultaneously placed at the ends of a tube of length L = 24 cm, as shown in the figure. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of 300 K. Vapours of X and Y react to form a product which is first observed at a distance *d* cm from the plug soaked in X. Take X and Y to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours.



Answer the following questions:

D6. The value of *d* in cm (shown in the figure), as estimated from Grahams law, is
(*a*) 8 (*b*) 12
(*c*) 16 (*d*) 20

D7. The experimental value of *d* is found to be smaller than the estimate obtained using Graham's law. This is due to
(*a*) larger mean free path of X as compared to that of Y
(*b*) larger mean free path of Y as compared to that of X
(*c*) increased collision frequency of Y with the inert gas as compared to that of X with the inert gas
(*d*) increased collision frequency of X with the inert gas as compared to that of Y with the inert gas.
(*JEE Advance 2014*)

Answers

Passage I. **D1.** *(a)* **D2.** *(d)* **D3.** *(c)* **D4.** *(b)* **D5.** *(c)* **Passage II.** **D6.** *(c)* **D7.** *(d)*

Assertion Reason Type Questions

The questions given below consist of an Assertion and the Reason. Use the following key to choose the appropriate answer.
(*a*) If both assertion and reason are CORRECT and reasson is the corect explanation of the assertion.
(*b*) If both assertion and reason are CORRET, but reason is NOT THE CORRECT explanation of the assertion.
(c) If assertion is CORRECT, but reason is INCORRECT.
(d) If assertion is INCORRECT, but reason is CORRECT.
(e) If both assertion and reason are INCORRECT.

1. Assertion : The value for van der Waal's constant '*a*' is higher for ammonia than for nitrogen.
Reason : Intermolecular hydrogen bonding is present in ammonia.

2. Assertion : Ligquefaction of H_2 and He are very difficult.
Reason : Critical temperature of H_2 and He gases are high.

3. Assertion : The pressure of ideal gases is always less than the pressure of real gases.
Reason : The intermolecular forces of attraction in ideal gases are less than those of real gases.

4. Assertion : For a certain amount of gas, the product *p*V is always constant.
Reason : This is statement of Charle's law

5. Assertion : The root mean square velocity of an ideal gas at constant pressure varies with density as $1\sqrt{d}$.
Reason : Average kinetic energy of a gas is directly proportional to the absolute temperature.

6. Assertion : At low pressure, van der Waal's equation may be expressed as
$$pV = RT - \frac{a}{V}$$
Reason : At low pressure *b* can be neglected in comparision to V.

7. Assertion : Compressibility factor ideal gases is one.
Reason : For ideal gases $pV = nRT$ equation is obeyed.

Answers

1. *(a)* **2.** *(c)* **3.** *(d)* **4.** *(e)* **5.** *(b)* **6.** *(a)* **7.** *(a)*

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8. **Assertion :** At critical point, the densities of gaseous and liquid states become same.

   Reason : At critical point, gases behave ideally.

9. **Assertion :** The temperature at which vapour pressure of a liquid is equal to the external pressure is called boiling temperature.

   Reason : At high altitude atmospheric pressure is high. *(NCERT Exemplar Problem)*

10. **Assertion :** The rate of effusion of O_2 is less than that of N_2.

    Reason : Molecular size of nitrogen is smalller than oxygen.

Answers

8. *(a)* **9.** *(c)* **10.** *(c)*

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.

	p	q	r	s
A	(p)	(q)	(r)	(s)
B	(p)	(q)	(r)	(s)
C	(p)	(q)	(r)	(s)
D	(p)	(q)	(r)	(s)

If the correct matches are A-*q*, A-*r*, B-*p*, B-*s*, C-*r*, C-*s* and D-*q*, then the correctly bubbled matrix will look like the following:

1. Match the gas law given in Column I with its description given in Column II.

Column I	Column II
(A) Charles' law	(*p*) $V \propto n$ (p and T constant)
(B) Boyle's law	(*q*) $V \propto \frac{1}{T}$ (p and n constant)
(C) Avogadro law	(*r*) $p_i = x_i\, p_{total}$ (at constant V and T)
(D) Dalton's law	(*s*) pV is constant (constant T and n)

2. Match the type of intermolecular forces given in Column I with the appripriate example given in Column II.

Column I	Column II
(A) London forces	(*p*) NH_3 molecules
(B) Kessom forces	(*q*) I_2 and NO_3^- ion
(C) Dipole induced –dipole forces	(*r*) SiH_4 molecule
(D) Hydrogen bonding	(*s*) HCl molecules

Answers

(1): (A) – (*q*) (B) – (*s*) (C) – (*p*) (D) – (*r*)

(2) : (A) – (*r*) (B) – (*p*), (*s*) (C)– (*q*) (D) – (*p*)

Integer Type Questions

Ingeger Type : The answer to each of the following question is a **single-digit**-integer ranging from 0 to 9.

1. At 400 K, the root mean square speed (rms) of a gas X (molecular weight = 60) is equal to most probable speed of gas Y at 60 K. The molecular weight of the gas Y is *(I.I.T. 2009)*
2. The temperature of 4.0 mol of an ideal gas occupying 5 dm^3 at 3.32 bar (R = 0.083 bar dm^3 K^{-1} mol^{-1}) is $n \times 10$ K. The value of n is
3. At the same pressure, the rate of diffusion of a gas at 927°C will be ... times that at 27°C.
4. Pressure of 1 g of an ideal gas at 27°C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at the same temperature, pressure becomes 3 bar. The number of times the molar mass of B as that of molar mass of A is
5. If pressure of an ideal gas is reduced to 1/4, then volume of the gas at the same temperature will become .... times.
6. A gas taken in a closed vessel is heated from 27°C to 627°C. The pressure of the gas will become .... times the original pressure.

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7. The average speed of gas is expressed as, $\mu_{av} = \sqrt{\frac{xRT}{\pi M}}$, the value of x is

8. If the value of Avogadro number is 6.023×10^{23} mol^{-1} and the value of Boltzman constant is 1.380×10^{-23} JK^{-1}, then the number of significant digits in the calculated value of the universal gas constant is
(*JEE Advance 2014*)

9. The diffusion coefficient of an ideal gas is proportional to its mean free path and mean speed. The absolute temperature of an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increases x times. The calue of x is
(*JEE Advance 2016*)

Answers

1. (4) **2.** (5) **3.** (2) **4.** (4) **5.** (4) **6.** (3) **7.** (8) **8.** (4) **9.** (4)

NCERT Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

1. A person living in Shimla observed that cooking food without using pressure cooker takes more time. The reason for this observation is that at high altitude :
   (*a*) pressure increases
   (*b*) temperature increases
   (*c*) pressure decreases
   (*d*) temperature increases

2. Which of the following property of water can be used to explain the spherical shape of rain droplets ?
   (*a*) viscosity
   (*b*) surface tension
   (*c*) critical phenomena
   (*d*) pressure

3. A plot of volume (V) versus temperature (T) for a gas at constant pressure is a straight line passing through the origin. The plots at different values of pressure are in the figure shown in Fig. 1. Which of the following order of pressure is correct for this gas ?
   (*a*) $p_1 > p_2 > p_3 > p_4$
   (*b*) $p_1 = p_2 = p_3 = p_4$
   (*c*) $p_1 < p_2 < p_3 < p_4$
   (*d*) $p_1 < p_2 = p_3 < p_4$

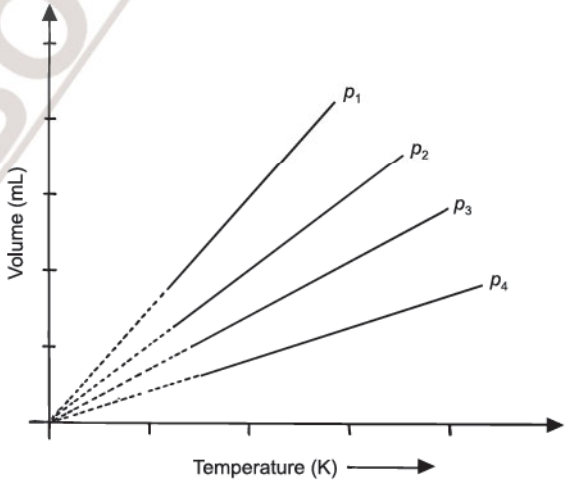

Fig. 1.

4. The interaction energy of London force is inversely proportional to sixth power of the distance between two interacting particles but their magnitude depends upon
   (*a*) charge of interacting particles
   (*b*) mass of interacting particles
   (*c*) polarisability of interacting particles
   (*d*) strength of permanent dipoles in the particles.

5. Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of dipoles possess 'partial charges'. The partial charge is
   (*a*) more than unit electronic charge
   (*b*) equal to unit electronic charge
   (*c*) less than unit electronic charge
   (*d*) double the unit electronic charge

Answers

1. (*c*) **2.** (*b*) **3.** (*c*) **4.** (*c*) **5.** (*c*)

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6. The pressure of a 1:4 mixture of dihydrogen and dioxygen enclosed in a vessel is one atmosphere. What would be the partial pressure of dioxygen ?

(*a*) 0.8×10^5 atm (*b*) 0.008 Nm^{-2}

(*c*) 8×10^4 Nm^{-2} (*d*) 0.25 atm

7. As the temperature increases, average kinetic energy of molecules increases. What would be the effect of increase of temperature on pressure provided the volume is constant ?

(*a*) increases (*b*) decreases

(*c*) remains same (*d*) becomes half

8. Gases possess characteristic critical temperature which depends upon the magnitude of intermolecular forces between the particles. Following are the critical temperatures of some gases.

Gases	H_2	He	O_2	N_2
Critical temperature in Kelvin	33.2	5.3	154.3	126

From the above data what would be the order of liquefaction of these gases ? Start writing the order from the gas liquefying first.

(*a*) H_2, He, O_2, N_2 (*b*) He, O_2, H_2, N_2

(*c*) N_2, O_2, He, H_2 (*d*) O_2, N_2, H_2, He

9. What is SI unit of viscosity coefficient (η) ?

(*a*) Pascal (*b*) Nsm^{-2}

(*c*) km^{-2} s (*d*) N m^{-2}

10. Atmospheric pressures recorded in different cities are as follows :

Cities	**Shimla**	**Bangalore**	**Delhi**	**Mumbai**
p in N/m^2	1.01×10^5	1.2×10^5	1.02×10^5	1.21×10^5

Consider the above data and mark the place at which liquid will boil first.

(*a*) Shimla (*b*) Bangalore

(*c*) Delhi (*d*) Mumbai

11. Which cruve in Fig. 2 (shown below) represents the curve of ideal gas ?

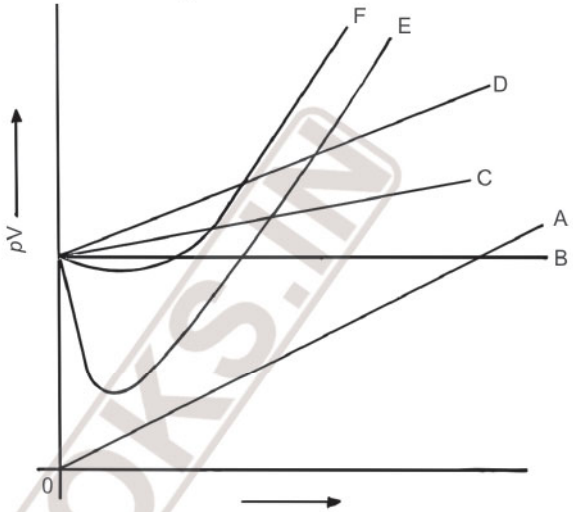

Fig. 2.

(*a*) B only (*b*) C and D only

(*c*) E and F only (*d*) A and B only

12. Increase in kinetic energy can overcome intermolecular forces of attraction. How will the viscosity of liquid be affected by the increase in temperature ?

(*a*) Increase

(*b*) No effect

(*c*) Decrease

(*d*) No regular pattern will be followed

13. How does the surface tension of a liquid vary with increase in temperature ?

(*a*) Remains same

(*b*) Decreases

(*c*) Increases

(*d*) No regular pattern will be followed

Answers

6. (*c*) **7.** (*a*) **8.** (*d*) **9.** (*b*) **10.** (*a*) **11.** (*a*) **12.** (*c*) **13.** (*b*)

Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

14. With regard to the gaseous state of matter which of the following statements are correct ?

(*a*) Complete order of molecules

(*b*) Complete disorder of molecules

(*c*) Random motion of molecules

(*d*) Fixed position of molecules

15. Which of the following figures does **not** represent 1 mole of dioxygen gas at STP ?

(*a*) 16 grams of gas

(*b*) 22.7 litres of gas

(*c*) 6.022×10^{23} dioxygen molecules

(*d*) 11.2 litres of gas

16. Under which of the following two conditions applied together, a gas deviates most from the ideal behaviour?

(*a*) Low pressure (*b*) High pressure

(*c*) Low temperature (*d*) High temperature

17. Which of the following changes decrease the vapour pressure of water kept in a sealed vessel ?

(*a*) Decreasing the quantity of water

(*b*) Adding salt to water

(*c*) Decreasing the volume of the vessel to one-half

(*d*) Decreasing the temperature of water

Answers

14. (*b*, *c*) **15.** (*a*, *d*) **16.** (*b*, *c*) **17.** (*b*, *d*)

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Matching Type Questions

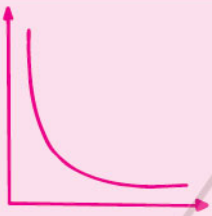
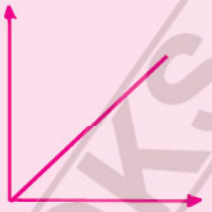
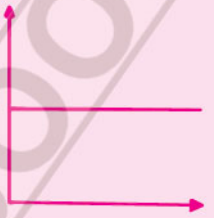
18. Match the graphs between the following variables with their names :

Graphs	*Names*
(*i*) Pressure vs temperature graph at constant molar volume.	(*a*) Isotherms
(*ii*) Pressure vs volume graph at constant temperature.	(*b*) Consent temperature curve
(*iii*) Volume vs temperature graph at constant pressure.	(*c*) Isochores
	(*d*) Isobars

19. Match the following gas laws with the equation representing them.

(*i*) Boyle's law	(*a*) $V \propto n$ at constant T and p
(*ii*) Charle's law	(*b*) $p_{Total} = p_1 + p_2 + p_3 + ...+$ at constant T,V
(*iii*) Dalton's law	(*c*) $\frac{pV}{T}$ = Constant
(*iv*) Avogadro law	(*d*) $V \propto T$ at constant n and p
	(*e*) $p \propto \frac{1}{V}$ at constant n and T

20. Match the following graphs of ideal gas with their coordinates :

Graphical representation	*x and y co-ordinates*
(*i*) 	(A) pV vs. V
(*ii*) 	(B) p vs. V
(*iii*) 	(C) p vs. $\frac{1}{V}$

Answers

18. (*i*) – (*c*); (*ii*) – (*a*); (*iii*) – (*d*), **19.** (*i*) – (*e*); (*ii*) – (*d*); (*iii*) – (*b*); (*iv*) – (*a*), **20.** (*i*) – (*b*); (*ii*) – (*c*); (*iii*) – (*a*)

Assertion and Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

(*a*) Both A and R are true and R is the correct explanation of A.
(*b*) Both A and R are true but R is not the correct explanation of A.
(*c*) A is true but R is false.
(*d*) A is false but R is true.

21. Assertion (A) : Three states of matter are the result of balance between intermolecular forces and thermal energy of the molecules.
Reason (R) : Intermolecular forces tend to keep the molecules together but thermal energy of molecules tends to keep them apart.

22. Assertion (A) : At constant temperature, pV vs V plot for real gases is not a straight line.
Reason (R) : At high pressure all gases have $Z > 1$ but at intermediate pressure most gases have $Z < 1$.

23. Assertion (A) : The temperature at which vapour pressure of a liquid is equal to the external pressure is called boiling temperature.
Reason (R) : At high altitude atmospheric pressure is high.

24. Assertion (A) : Gases do not liquefy above their critical temperature, even on applying high pressure.
Reason (R) : Above critical temperature, the molecular speed is high and intermolecular attractions cannot hold the molecules together because they escape because of high speed.

25. Assertion (A) : At critical temperature liquid passes into gaseous state imperceptibly and continuously.
Reason (R) : The density of liquid and gaseous phase is equal to critical temperature.

26. Assertion (A) : Liquids tend to have maximum number of molecules at their surface.

Answers

21. (*a*) **22.** (*b*) **23.** (*c*) **24.** (*a*) **25.** (*a*) **26.** (*d*)

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Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A2. (*c*) : $x(O_2) = \frac{4}{1+4} = 0.8$

$p(O_2) = 1 \times 0.8$ atm

$= 0.8 \times 1.01325 \times 10^5$ Nm^{-2}

$= \mathbf{8 \times 10^4\ Nm^{-2}}$

A3. (*b*) : $\frac{p_1}{T_1} = \frac{p_2}{T_2}$

$\frac{p_1}{300} = \frac{p_2}{600} \quad \therefore\ p_2 = \frac{600}{300} p_1$

$= 2p_1$

i.e. pressure becomes double.

A4. (*b*) : $V_1 = 283$ mL, $T_1 = 273 + 10 = 283$ K

$V_2 = ?$ $T_2 = 273 + 20 = 293$ K

$\frac{V_1}{T_1} = \frac{V_2}{T_2}$ (at constant p)

$V_2 = \frac{V_1}{T_1} \times T_2 = \frac{283 \times 293}{283} = \mathbf{293\ mL.}$

A5. (*b*) : $p_1V_1 = p_2V_2$

$1 \times V = 2 \times V_2$

$\therefore\ V_2 = \mathbf{V/2}$

A6. (*d*) : Moles of $CH_2 = \frac{w}{16}$

Moles of $H_2 = \frac{w}{2}$

(w is the mass of CH_4 and H_2)

$\therefore\ pH_2 = \frac{\frac{w}{2}}{\frac{w}{2} + \frac{w}{16}} \times P$

$= \frac{w}{2} \times \frac{16}{9w} \times P = \mathbf{\frac{8}{9}\ P.}$

A7. (*b*) : $M = \frac{dRT}{p} = \frac{1.964 \times 0.082 \times 273}{76/76} = 44$

$\therefore$ It corresponds to CO_2.

A9. (*b*) : $p_1V_2 = p_2V_2$

$p_1 \times V_1 = p_2 \times 3V_1$

$\therefore\ p_2 = \mathbf{p_1/3.}$

A10. (*a*) : $T_1 = 273 + 37 = 310$ K

Initial moles of air = n mol

Moles of air left $= n - \frac{3}{5}n = \frac{2}{5}n$

Final temp. $= \frac{310 \times 5}{2} = 775$ K

or $775 - 273 = \mathbf{502°C.}$

A11. (*a*) : Average V.D. of air $= \frac{4 \times 14 + 1 \times 16}{5} = \mathbf{14.4}$

A13. (*c*) : Partial pressure of a gas

= Mole of fraction × Total pressure

For partial pressures to be equal

$x(SO_3) = x(N_2)$

$x(SO_3) = \frac{W_1/80}{W_1/80 + W_2/28}$

$x(N_2) = \frac{W_2/28}{W_1/80 + W_2/28}$

$\frac{W_1}{80} = \frac{W_2}{28}$

$\frac{W_1}{W_2} = \frac{80}{28} = \mathbf{\frac{20}{7}}$

A14. (*a*) :

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial conc.	1		0
At equilibrium	1 − 0.20		0.40

Mol. wt. of mixture $= \frac{0.80 \times 92 + 0.4 \times 46}{1.2}$

$= 76.66$

Now $\rho = \frac{pM}{RT} = \frac{1 \times 76.66}{0.082 \times 300} = \mathbf{3.1\ gL^{-1}}$

A15. (*c*) : $r \propto p$ and $\propto \frac{1}{\sqrt{\rho}}$ or $\propto \frac{1}{\sqrt{M}}$

$\therefore\ \frac{r_A}{r_B} = \frac{p_A}{p_B}\left(\frac{M_B}{M_A}\right)^{1/2}$

A17. (*a*) : $x_{H_2O} = 0.0265$, $p_{total} = 0.980$

$pH_2O = x_{H_2O} \times p_{total} = 0.0265 \times 0.980 = 0.026$ bar

% humidity $= \frac{pH_2O \text{ in air}}{\text{Vap. press. of } H_2O} \times 100$

$= \frac{0.026}{0.0315} \times 100 = \mathbf{82.5}$

A18. (*d*) : Molar volume from pyknometer density

$= \frac{M}{2.165 \times 10^3}\ m^3$

Molar volume from X-ray density

$= \frac{M}{2.178 \times 10^3}\ m^3$

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$\therefore$ Volume unoccupied

$$\left(\frac{1}{2.165}-\frac{1}{2.178}\right)\frac{M}{10^3}m^3$$

Fraction unoccupied

$$=\left(\frac{1}{2.165}-\frac{1}{2.178}\right)\Big/\frac{1}{2.165}$$

$$=\frac{0.013}{2.165\times178}\times2.165$$

$$=\mathbf{5.96\times10^{-3}}$$

A19. (*d*) : $\frac{r_{CH_4}}{r_x}=\sqrt{\frac{M_x}{M_{CH_4}}}$ $\therefore$ $2=\sqrt{\frac{M_x}{16}}$

$M_x = 16\times4 = \mathbf{64}$

A20. (*b*) : Boyle's law is

$pV = \text{Constant}$

Differentiating this equation,

$pdV + Vdp = 0$ or $Vdp = -pdV$

or $\frac{dp}{p} = -\frac{dV}{V}$

A22. (*b*) : u_{av} of $O_2 = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8RT}{\pi\times32}}$

u_{rms} of $N_2 = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3RT}{28}}$

$$\frac{u_{av}}{u_{rms}} = \sqrt{\frac{8RT}{\pi\times32}}\times\sqrt{\frac{28}{3RT}} = \left(\frac{7}{3\pi}\right)^{\frac{1}{2}}$$

A23. (*b*) : Since temperature is same, the kinetic energies of two samples of gases A and B will be same.

Now, $v_A = 4v_B$

$\therefore \frac{1}{2}M_A(4v_B)^2 = \frac{1}{2}M_B{v^2}_B$

$\frac{M_A}{M_B} = \frac{1}{16}$.

A24. (*b*) : $\sqrt{\frac{3RT}{16}} = 2\times\sqrt{\frac{3R\times273}{16}}$

$T = 4\times273$

$T = 1092$ or $819°C$

A26. (*d*) : $\frac{1}{2}m_1{v^2}_1 = \frac{1}{2}m_2{v^2}_2$

or $m_1{v^2}_1 = m_2{v^2}_2$

A27. (*c*) : $u = \sqrt{\frac{3RT}{M}}$

$$\frac{u(H_2)}{u(N_2)} = \sqrt{\frac{T(H_2)}{M(H_2)}\times\frac{M(N_2)}{T(N_2)}}$$

$$\sqrt{7} = \sqrt{\frac{T(H_2)}{T(N_2)}\times\frac{28}{2}}$$

$$7 = \frac{T(H_2)}{T(N_2)}\times14$$

$T(N_2) = 2T(H_2)$

i.e. $T(N_2) > T(H_2)$

or $T(H_2) < T(N_2)$

A28. (*b*) : $K.E. = \frac{3}{2}nRT$

$\frac{3}{2}\times0.40\times500 = \frac{3}{2}\times0.30\times T$

$\therefore T = \frac{0.40\times500}{0.30}$

$= \mathbf{666.7\ K}$

A34. (*c*) : At low pressure, volume is sufficiently large so that b can be neglected in comparison to V so that

$\left(p+\frac{a}{V^2}\right)(V-b) = RT$

or $\left(p+\frac{a}{V^2}\right)V = RT$

$pV + \frac{a}{V} = RT$

or $pV = RT - \frac{a}{V}$

A41. (*c*) : Water has the maximum surface tension because of strong intermolecular forces.

B. *mcq from competitive examinations*

B1. (*b*) : Let mass of $SO_3 = x$, mass of $O_2 = x$

Moles of $SO_3 = \frac{x}{80}$, Moles of $O_2 = \frac{x}{32}$

Mole fraction of $SO_3 = \frac{\frac{x}{80}}{\frac{x}{80}+\frac{x}{32}}$

Mole fraction of $O_2 = \frac{\frac{x}{32}}{\frac{x}{80}+\frac{x}{32}}$

Ratio of mole fractions, $\frac{x(SO_3)}{x(O_2)} = \frac{32}{80} = \frac{2}{5}$

Since partial pressures are proportional to mole fraction

$\therefore$ Ratio of partial pressures = **2 : 5**

B3. (*d*) : Rate of diffusion $\propto \frac{1}{\sqrt{M}}$

Rate of diffusion of NH_3 is greater than HCl. Hence white ring of NH_4Cl will be formed near HCl.

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B4. (*b*) : According to Boyle's law, at constant temperature,

$p_1V_1 + p_2V_2 = p_{mix} \times V_{mix}$

$4 \times 4 + 6 \times 6 = p_{mix} \times (6 + 4)$

$\therefore p_{mix} = \frac{52}{10} = \mathbf{5.2\ bar}$

B5. (*c*) : Kinetic energy of gaseous molecules depends only on temperature.

B6. (*a*) : The gas having higher critical temperature liquefies first.

B7. (*b*) : $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$

$p_1 = 1.5$ atm

$T_1 = 15°\ C = (15 + 273)\ K = 288\ K$

$p_2 = 1.0$ atm

$T_2 = 25°\ C = (25 + 273)\ K = 298\ K$

$\therefore \frac{1.5 \times V_1}{288} = \frac{1 \times V_2}{298}$

$\therefore V_2 = \frac{V_1 \times 298 \times 1.5}{288} = 1.55\ V_1 \approx \mathbf{1.6\ V_1}$

B9. (*a*) : Mass of glass vessel = 50 g

Mass of liquid = 144 – 50 = 94 g

Density of liquid = 0.47 g mL^{-1}

$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$

$\therefore$ Volume of glass vessel, $V = \frac{\text{Mass}}{\text{Density}}$

$= \frac{94g}{0.47g\ mL^{-1}}$

$= 200\ mL = \mathbf{0.2\ L}$

Pressure of gas, p = 760 mm Hg = 1 atm.

Temperature of gas, T = 300 K

Mass of gas in glass vessel = (50.5 – 50)g = 0.5 g

$pV = nRT$ or $pV = \frac{m}{M}RT$

$1\ atm \times 0.2\ L = \frac{0.5g}{M} \times 0.0821\ L\ atm.\ K^{-1}\ mol^{-1} \times 300\ K$

$\therefore M = \frac{0.5g \times 0.0821\ L\ atm\ K^{-1}mol^{-1} \times 300\ K}{1atm \times 0.2\ L}$

$= 61.575\ g\ mol^{-1}$

B10. (*c*) : $V = 2.24 \times 10^{-3}\ m^3 = 2.24\ L$

$m = 4.4$ g

$T = 273.15$ K

$p = 101.325\ kPa$

$= 101325\ Pa = 1\ atm$

$pV = nRT$ or $pV = \frac{m}{M}RT$

$\therefore 1\ atm \times 2.24\ L = \frac{4.4g}{M} \times 0.0821\ L\ atm\ K^{-1}\ mol^{-1} \times 273.15\ K$

$\therefore M = 44.05\ g\ mol^{-1}$

Therefore, the gas is C_3H_8

B11. (*e*) : The volume of bubble at bottom of the lake becomes 8 times. This means that the pressure at the bottom of the lake is 8 times the pressure at the surface. Therefore, pressure due to depth of lake is 8 × 10 – 10 = **70 m**.

B12. (*a*) : $n(CO) = n(N_2)$

$p(CO) + p(N_2) = 1$ atm

Mole fraction of N_2, $x_{N_2} = \frac{1}{1+1} = 0.5$

$p(N_2) = p \times x_{N_2} = 1 \times 0.5 = \mathbf{0.5\ atm}$.

B13. (*b*) : $\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$

$\frac{V/20}{V/10} = \sqrt{\frac{M_B}{49}}$ $\therefore M_B = 49 \times \frac{1}{4} = \mathbf{12.25\ u}$

B14. (*d*) : Average velocity = $\sqrt{\frac{8RT}{\pi M}}$

or u_{av} or $\sqrt{T}$

$\frac{(u_{av})_2}{(u_{av})_1} = \sqrt{\frac{2T}{T}} = \mathbf{1.414}$

B15. (*a*) : Moles of $O_2 = \frac{64}{32} = 2$

Moles of Ne = $\frac{60}{20} = 3$

Mole fraction of $O_2 = \frac{2}{2+3} = 0.4$

$p(O_2) = 0.4 \times 10 = 4$ bar

Mole fraction of Ne = $\frac{3}{2+3} = 0.6$

$p(Ne) = 0.6 \times 10 = 6$ **bar.**

B16. (*b*) : Surface tension of a liquid decreases with increase in temperature because of decrease in intermolecular forces of attraction.

B17. (*e*) : CO_2 has the highest critical temperature among these.

B18. (*d*) : $\frac{r_A}{r_B} = \frac{\frac{V_A}{t_A}}{\frac{V_B}{t_B}} = \sqrt{\frac{M_B}{M_A}}$

For same volume

$\frac{t_B}{t_A} = \sqrt{\frac{M_B}{M_A}}$

$\frac{200}{150} = \sqrt{\frac{M_B}{36}}$

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$$\frac{M_B}{36} = \left(\frac{200}{150}\right)^2 = 1.78$$

$$M_B = 36 \times 1.78 = \mathbf{64}$$

B19. (*b*) : Van der Waals' equation is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

At high pressure, $\frac{a}{V^2}$ can be neglected so that

$$p(V - b) = RT$$

$$pv - pb = RT$$

$$\frac{pV}{RT} - \frac{pb}{RT} = 1$$

or $$\frac{pV}{RT} = 1 + \frac{pb}{RT}$$

$\therefore$ $$Z = 1 + \frac{pb}{RT}$$

B20. (*d*) : Average K.E. for 1 mol of gas = $\frac{3}{2}$ RT

Average K.E. for 1 molecule = $\frac{3}{2}\frac{RT}{N_A}$.

B21. (*c*) : p_A = 1 atm. p_B = 2 – 1 = 1 atm.

At same temperature and pressure, the two gases have same number of moles i.e.,

$$n_A = n_B$$

$$\frac{w_A}{M_A} = \frac{w_B}{M_B}$$

or $$\frac{M_A}{M_B} = \frac{w_A}{w_B} = \frac{4}{6} = \frac{2}{3}$$ *i.e.*, **2 : 3.**

B22. (*e*) : No. of atoms in 800 mg or 800×10^{-3} g of Ca

$$= \frac{800 \times 10^{-3}}{40} \times N_A = 0.02\, N_A$$

N_A atoms of neon are present in 22.4 L

$\therefore$ 0.02 N_A atoms of neon are present in

$$= \frac{22.4}{N_A} \times 0.02\, N_A = 0.448 \text{ L}$$

or = **448 cm³.**

B23. (*c*) : The molecular collisions are elastic and not the molecules.

B24. (*b*) : NH_3 is polar molecule and hence has more attractive forces between its molecules.

B25. (*a*) : HCl is polar and He is non-polar and therefore, has dipole induced dipole interactions.

B26. (*c*) : Let the mass of H_2, O_2 and CH_4 taken be '*w*' gram.

$\therefore$ Number of moles of H_2, O_2 and CH_4 are $\frac{w}{2}$, $\frac{w}{32}$ and $\frac{w}{16}$ respectively.

According to Avogadro's law, ratio of volumes is equal to ratio of number of moles under identical conditions of temperature and pressure.

$\therefore$ ratio of volumes of $H_2 : O_2 : CH_4 = \frac{1}{2} : \frac{1}{32} : \frac{1}{16}$

= **16 : 1 : 2**

B27. (*e*) : For a mixture of non-reacting gases,

partial pressure $\propto$ no of moles

$$n_{He} : n_{O_2} : n_{SO_2} = \frac{1}{4} : \frac{1}{32} : \frac{1}{64}$$

Or

$\therefore$ $p_{He} : p_{O_2} : p_{SO_2}$ = **16 : 2 : 1**

B28. (*c*) : Easily liquifiable gases (water vapour) have higher critical temparature.

B29. (*c*) : Real gases show ideal behaviour at high temperature and low pressure.

B30. (*c*) : $\frac{r(H_2)}{r(O_2)} = \sqrt{\frac{M(O_2)}{M(H_2)}} = \sqrt{\frac{32}{2}} = \frac{4}{1}$

$\therefore$ $$r(O_2) = \frac{1}{4} r(H_2)$$

When $$r(H_2) = 1/2$$

$$r(O_2) = \frac{1}{4} \times \frac{1}{2} = \frac{1}{8}$$

B31. (*a*) : Van der Waals' constant (*a*) signifies intermolecular forces. Higher the value of (*a*) easier will be the liquefaction of the gas. So, NH_3 will be easily liquefied.

B32. (*d*) : Van der Waals' constant (*a*) corresponds to forces of attraction.

B33. (*c*) : At 273 K and 1 atm, volume of 1 mole of an ideal gas 22.4 L.

Volume at 373 K and 1 atm will be

$$V = \frac{RT}{p} = \frac{0.082 \times 373}{1} = \mathbf{30.58\ L}$$

B34. (*b*) : Let the mass of methane and oxygen be *x* g each.

$$\text{Moles of } CH_4 = \frac{x}{16}$$

$$\text{Moles of } O_2 = \frac{x}{32}$$

$$\text{Total moles} = \frac{x}{16} + \frac{x}{32} = \frac{3x}{32}$$

$$p_{O_2} = p_{total} \times x_{O_2}$$

$$\frac{p_{O_2}}{p_{total}} = x_{O_2} = \frac{\frac{x}{32}}{\frac{3x}{32}} = \mathbf{\frac{1}{3}}$$

B35. (*a*) : According to Boyle's law, *p*V = constant

or $$p_1V_1 = p_2V_2$$

If $$V_2 = V_1 + \frac{V_1 \times 10}{100} = 1.1\, V_1$$

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$$p_2 = \frac{p_1V_1}{V_2} = \frac{p_1 \times V_1}{1.1V_1} = 0.9\,p_1$$

$\therefore$ Pressure decreases by **10%.**

B36. (*c*) : According to Avogadro's law, equal volumes of gases contain equal number of molecules under similar conditions of temperature and pressure.

B37. (*d*) : r.m.s. velocity $= \sqrt{\frac{3P}{d}}$

$$= \sqrt{\frac{3\times1.2\times10^5\ \text{N m}^{-2}}{4\ \text{kg m}^{-3}}}$$

$$= \sqrt{\frac{3\times1.2\times10^5\ \text{kg ms}^{-2}\ \text{m}^{-2}}{4\ \text{kg m}^{-3}}}$$

$$= \mathbf{300\ ms^{-1}}$$

B38. (*d*) : $u_{r.m.s.} = \sqrt{\frac{3RT}{M}}$ $\therefore$ $u_{r.m.s.} \propto \sqrt{T}$.

For $u_{r.m.s.}$ to be doubled, temperature must be raised by 4 times.

$T = (50 + 273)\ K = 323\ K$

$\therefore$ $4T = 4 \times 323\ K = 1292\ K = (1292 - 273)\ C = 1019°\ C.$

B39. (*c*) : Density of a gas, $d = \frac{pM}{RT}$

or $$p = \frac{dRT}{M}$$

$\therefore$ $$p_A = \frac{d_ART}{M_A} \text{ and } p_B = \frac{d_BRT}{M_B}$$

Given that : $$d_A = 2d_B,\ M_A = \frac{M_B}{2}$$

$\therefore$ $$p_A = \frac{2d_BRT}{M_B/2} = \frac{4d_BRT}{M_B}$$

$\therefore$ $$\frac{p_A}{p_B} = \frac{4d_BRT/M_B}{d_BRT/M_B} = \frac{4}{1}$$

B40. (*b*) : $$\frac{r_{H_2}}{r_{Hydrocarbon}} = \sqrt{\frac{M_{Hydrocarbon}}{M_{H_2}}} = 3\sqrt{3}$$

$\therefore$ $$\sqrt{\frac{M_{Hydrocarbon}}{2}} = 3\sqrt{3}$$

$$\frac{M_{Hydrocarbon}}{2} = 27$$

$$M_{Hydrocarbon} = 2 \times 27 = \mathbf{54}$$

$\therefore$ $n = 4$ and hydrocarbon is C_4H_6

B42. (*b*) : $pV = nRT$

$$n = \frac{pV}{RT}$$

$p = 3170$ Pa

$R = 8.314 \times 10^3$ Pa dm^3 K^{-1} mol^{-1}

$V = 1\ dm^3$ (volume of vapours is same as that of flask)

$$n = \frac{3170\times1}{8.314\times10^3\times300}$$

$$n = \mathbf{1.27\times10^{-3}\ mol}$$

B43. (*d*) : Gases always form homogeneous mixture.

B45. (*d*) : Van der Waals' constant '*a*' is a measure of intermolecular forces of attraction and *b* is a measure of size of gas molecules. Larger the intermolecular forces of attraction and smaller the size of molecules, more will be the ease of liquefaction.

B46. (*a*) : $p_1V_1 = n_1RT_1$

$p_2V_2 = n_2RT_2$

or $$\frac{n_1}{n_2} = \frac{p_1V_1T_2}{p_2V_2T_1}$$

$$= \frac{1.5\times16.4\times500}{4.1\times5\times300} = \frac{2}{1}.$$

B47. (*d*) : $$C^* : \bar{C} : C = \sqrt{\frac{2\,RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{2} : \sqrt{\frac{8}{3.14}} : \sqrt{3}$$

$$= \mathbf{1 : 1.128 : 1.225}$$

B48. (*c*) : According to ideal gas equation

$pV = nRT$

or $$V = \frac{nRT}{p}$$

For 1 mole of ideal gas, the equation is, $V = \frac{RT}{p}$

$\therefore$ the slope (X) of V vs T curve $= \frac{R}{p}$

or $R = p \times XL\ mol^{-1}K^{-1}$

Since $p = 2$ atm

$\therefore$ $R = 2X$ L atm mol^{-1} K^{-1}

B49. (*b*) : Rate of diffusion $= \frac{\text{Volume of gas diffused}}{\text{Time taken}}$

or $$\frac{r_{H_2}}{r_{O_2}} = \frac{V_{H_2} \times t_{O_2}}{V_{O_2} \times t_{H_2}}$$

Also, $$\frac{r_{H_2}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{H_2}}}$$

$\therefore$ $$\sqrt{\frac{M_{O_2}}{M_{H_2}}} = \frac{V_{H_2}}{V_{O_2}} \times \frac{t_{O_2}}{t_{H_2}}$$

$$\sqrt{\frac{32}{2}} = \frac{200 \times t_{O_2}}{50 \times 30}$$

or $$t_{O_2} = \frac{4\times50\times30}{200} = \mathbf{30\ min}.$$

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B50. (*a*) : More the value of *a*, more will be the forces of attraction between the gaseous molecules and hence, more easily the gas will be liquefied.

B51. (*a*) : $pV = nRT$

$$p = \frac{nRT}{V} = \frac{2 \times 0.0821 \times 500}{41}$$

$$= \mathbf{2\ atm}$$

B52. (*a*) : Let the unknown gaseous oxide be '*x*'

$$\rho_x = p\frac{M_x}{RT} = \frac{2 \times M_x}{RT}$$

and $$\rho_{O_2} = \frac{pM_{O_2}}{RT} = \frac{5 \times 32}{RT}$$

Given that $\rho_x = \rho_{O_2}$

$$\therefore \quad \frac{2 \times M_x}{RT} = \frac{5 \times 32}{RT}$$

or $$M_x = \mathbf{80\ g\ mol^{-1}}$$

B53. (*d*) : Density of a gas, $\rho = \frac{pM}{RT}$ or $\rho \propto \frac{p}{T}$

By using this relation, density is maximum at 4 atm and 500 K.

B54. (*c*) : $\left(p + \frac{a}{V^2}\right)(V - b) = RT$

At low pressure, the volume is sufficiently large and therefore, *b* can be neglected in comparison to V so that

$$\left(p + \frac{a}{V^2}\right)V = RT$$

$$pV + \frac{a}{V} = RT$$

or $$pV = RT - \frac{a}{V}$$

$$\frac{pV}{RT} = 1 - \sqrt{\frac{3RT}{M}} \quad \text{or} \quad Z = 1 - \frac{a}{RTV}$$

B55. (*b*) : Initially, $p_1 = 1$ atm, $T_1 = 300$ K, $n_1 = 1$ mol

Finally, $p_2 = ?$, $T_2 = 600$ K

When 20% of N_2O_4 decomposes to NO_2, then

	$N_2O_4(g)$	$\rightleftharpoons$	$2\,NO_2(g)$
Initial conc.	1 mol		0
Final conc.	= 1 (1–0.2)		2 (0.2)
	= 0.8 mol		0.4 mol

Total number of moles after decomposition

$= 0.8 + 0.4$

$= 1.2$ mol

From ideal gas equation,

$$\frac{p_1V}{p_2V} = \frac{n_1RT_1}{n_2RT_2}$$

$$\frac{1 \times V}{p_2 \times V} = \frac{1 \times R \times 300}{1.2 \times R \times 600}$$

$$p_2 = \frac{1.2 \times 600}{300} = \mathbf{2.4\ atm}$$

B57. (*b*) : Gases can be liquefied if temperature is lower than critical temperature ($T < T_c$) and pressure is greater than critical pressure ($p > p_c$)

B58. (*b*) : $$\mu_{rms} = \sqrt{\frac{3RT}{M}}$$

$$\frac{\mu_{rms}(CO)}{\mu_{rms}(N_2)} = \sqrt{\frac{3RT\,(CO)}{M\,(CO)} \times \frac{M(N_2)}{3\,RT\,(N_2)}}$$

$$\frac{1000}{\mu_{rms}(N_2)} = \sqrt{\frac{300}{28} \times \frac{28}{600}} = \frac{1}{\sqrt{2}}$$

$$\therefore \quad \mu_{rms}(N_2) = 1000 \times \sqrt{2} = 1000 \times 1.414$$

$$= \mathbf{1414\ ms^{-1}}$$

B61. (*e*) : Dipole-dipole interaction energy between polar molecules in solids is proportional to $1/r^3$.

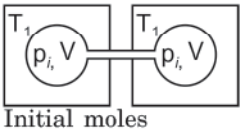
B62. (*a*) : Critical density = $0.1\,g\,cm^{-3}$

$$\text{Critical volume} = \frac{\text{Molecular mass}}{\text{Critical density}}$$

$$= \frac{39\,g\ mol^{-1}}{0.1\,g\ cm^{-3}}$$

$$= 390\ cm^3\ mol^{-1} = \mathbf{0.39\ L\ mol^{-1}}$$

B64. (*c*) :



Initial moles

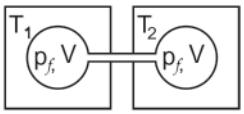
No. of moles in first container, $n_1 = \frac{p_iV}{RT_1}$

No. of moles in second container, $n_2 = \frac{p_iV}{RT_1}$

Total moles in two containers.

$$n_1 + n_2 = \frac{p_iV}{RT_1} + \frac{p_iV}{RT_1} = \frac{2p_iV}{RT_1}$$

After heating one of the bulbs to T_2



No. of moles in first container, $n_1' = \frac{p_fV}{RT_1}$

No. of moles in second container, $n_2' = \frac{p_fV}{RT_2}$

Total moles in two containers

$$n_1' + n_2' = \frac{p_fV}{RT_1} + \frac{p_fV}{RT_2}$$

Since $n_1 + n_2 = n_1' + n_2'$

$$\frac{2p_iV}{RT_1} = \frac{p_fV}{RT_1} + \frac{p_fV}{RT_2}$$

$$\frac{2p_iV}{RT_1} = \frac{p_fV}{R}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)$$

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$$= \frac{p_f V}{R}\left(\frac{T_1 + T_2}{T_1\ T_2}\right)$$

$$2p_i = p_f\left(\frac{T_1 + T_2}{T_2}\right)$$

$$p_f = 2p_i\left(\frac{T_2}{T_1 + T_2}\right)$$

B65. (*a*) : For ideal gases,

$$pV = nRT = \frac{w}{M}RT \qquad (\because n = \frac{w}{M})$$

For same mass of gases at constant temperature, w RT is constant (say K)

$$pV = \frac{K}{M}$$

Taking log on both sides,

$$\log p + \log V = \log\frac{K}{M}$$

or $$\log V = -\log P + \log\frac{K}{M}$$

Comparing with equation of straight line ($y = mx + c$)

For ideal gas(1), Intercept(1) = $\log\frac{K}{M_1}$

For ideal gas(2), Intercept(2) = $\log\frac{K}{M_2}$

From graph,

$$\log\frac{K}{M_2} > \log\frac{K}{M_1}$$

or $$\frac{K}{M_2} > \frac{K}{M_1} \quad \therefore \mathbf{M_1 > M_2}$$

B66. (*b*): Surface tension,

$$r = \frac{\text{Force}}{\text{Length}}$$

$$= \frac{M^1L^1T^{-2}}{L^1} = M^1L^0T^{-2}$$

B67. (*b*) : Because of intermolecular forces of attraction, the observed pressure of the gas is less than the ideal pressure.

B69. (*c*) : The volume of the gas at 0 K will be zero. This means that gas will not exist at 0 K. Therefore, the pressure of the gas will be zero.

B70. (*b*) : $C_{av} = \sqrt{\frac{8RT}{\pi M}}$ and $C_{mp} = \sqrt{\frac{2RT}{M}}$

Now C_{av} (gas 1) = C_{mp} (gas 2)

$$\sqrt{\frac{8RT_1}{\pi M_1}} = \sqrt{\frac{2RT_2}{M_2}}$$

$$\frac{8T_1}{\pi M_1} = \frac{2T_2}{M_2} \text{ or } \frac{4T_1}{\pi \times 56} = \frac{T_2}{44}$$

$$\therefore \frac{T_1}{T_2} = \frac{56\times\pi}{44\times4} = \frac{56\times3.142}{44\times4} = 1$$

$\therefore$ $\mathbf{T_1 = T_2}$

B71. (*c*) : Van der Waals' gas equation is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

At low pressure, the volume is sufficiently large, so that b can be neglected in comparison to V.

$$\left(p + \frac{a}{V^2}\right)V = RT \qquad \text{or} \qquad pV + \frac{a}{V} = RT$$

or $$pV = RT - \frac{a}{V}$$

B73. (*d*) : Suppose w is the weight of both C_2H_6 and H_2 taken.
$M(C_2H_6) = 30$, $M(H_2) = 2$

$$\therefore n(C_2H_6) = \frac{w}{30}, \quad n(H_2) = \frac{w}{2}$$

$$p(H_2) = X_{H_2} \times p$$

$$= \left(\frac{w/2}{w/2 + w/30}\right)p$$

$$= \left(\frac{1/2}{1/2 + 1/30}\right)p$$

$$= \left(\frac{\frac{1}{2}}{\frac{15+1}{30}}\right)p$$

$$= \frac{1}{2}\times\frac{30}{16} = \frac{15}{16}p$$

$\therefore$ $pH_2 = \frac{15}{16}p$ or $pH_2 : p = \mathbf{15 : 16}$

B74. (*b*): A_2B_3 has hcp lattice.

If A forms hcp, then tetrahedral voids will be $2 \times 2 = 4$

Fraction occupied by B = $\frac{3}{4}$

If B forms hcp, then tetrahedral voids = $2 \times 3 = 6$

Fraction occupied by A = $\frac{2}{6} = \frac{1}{3}$

B75. (*a*): $V_A = 2V_B$

Compressibility factor, $Z_A = 3Z_B$

or $$\frac{p_A V_A}{n_A RT_A} = \frac{3p_B V_B}{n_B RT_B}$$

For equal number of moles, $n_A = n_B$ and same temperature $T_A = T_B$

$$p_A V_A = 3p_B V_A/2$$

or $$2p_A = 3p_B$$

B76. (*b*): $Z = \frac{pV}{nRT}$ or $\frac{pV}{nRT} < 1$

or $$pV_m < nRT$$

or $$1 \text{ atm} \times V_m < 1 \times 0.082 \times 273$$

or $$V_m < 22.4 \text{ L}.$$

B79. (*c*) : Vol. of 1 mol of ideal gas at 273 K and 1 atm is 22.4 L

$\therefore$ Vol. at 373 K and 1 atm pressure

$$V = \frac{RT}{p} = \frac{0.082\times373}{1}$$

$= 30.58 \text{ L} \approx \mathbf{30.6\ L.}$

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B81. (*c*) : $u_{r.m.s} = \sqrt{\frac{3RT}{M}}$

Average kinetic energy, $E = \frac{3}{2} nRT$

For 1 mole of a gas,

$$E = \frac{3}{2} RT$$

or $$RT = \frac{3}{2} E$$

$$\therefore \quad u_{r.m.s} = \sqrt{\frac{3 \times \frac{2}{3} E}{M}} = \sqrt{\frac{2E}{M}}$$

B82. (*b*): $\frac{r(He)}{r(CH_4)} = \sqrt{\frac{M(CH_4)}{M(He)}} = \sqrt{\frac{16}{4}} = 2$

B83. (*b*) : For gas B, b = 0 so that $Z = 1 - \frac{a}{VRT}$

$\therefore$ Z does not vary linearly with *p*

$\therefore$ (*b*) is not correct.

For gas A, $a = 0$, $Z = 1 + \frac{pb}{RT}$

$\therefore$ Z varies linearly with *p*

$\therefore$ (*a*) is correct.

Given the intersection data for gas C, it is possible to calculate '*a*' and '*b*'.

$\therefore$ (*c*) is correct choice.

All van der Waals gases like gas C give positive slope at high pressure

$\therefore$ (*d*) is correct.

Hence (*b*) is correct choice.

B85. (*c*) : For one mole of a real gas, van der Waals equation is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

when $b = 0$

$$\left(p + \frac{a}{V^2}\right)(V) = RT$$

or $$pV + \frac{a}{V} = RT$$

$$pV = RT - \frac{a}{V}$$

Therefore, *p*V vs 1/V graph is a straight line having slope = $-a$

Slope of the given line = $-a = \frac{y_2 - y_1}{x_2 - x_1}$

or $$-a = \frac{21.6 - 20.1}{2 - 3}$$

$$= -1.5 \text{ atm } L^2 \text{ mol}^{-2}$$

or $$a = \mathbf{1.5 \text{ atm } L^2 \text{ mol}^{-2}}$$

B86. (*d*) : For CH_3OH curve : decrease of surface tension progressively due to hydrophobic interaction.

For KCl curve : increase of surface tension because of intermolecular forces of attraction.

For $CH_3(CH_2)_{11}\ OSO_3^-Na^+$: decrease of surface tension before critical micelle concentration (CMC) and then almost unchanged.

C. *mcq with more than one correct answer*

C6. (*a,c,d*) : (*a*) van der Waals equation is :

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \text{ for 1 mole}$$

When V is very large, $V - b \approx V$ and

$p + \frac{a}{V^2} \approx p$ so that $pV = RT$ *i.e.* behaves similar to ideal gas

(*c*) van der Waals coefficients (*a*) and (*b*) are characteristic of a gas and are independent of temperature.

(*d*) Due to inward pull acting on a molecule striking the wall, the pressure decreases.

D. *mcq based on comprehension*

D1. (*a*) : For ideal gas, Z = 1

D4. (*b*) : $Z = \frac{V_{real}}{V_{ideal}}$

D5. (*c*) : For the gas D which shows only positive deviation, Z is always greater than 1. This is possible only if a/V^2 becomes negligible.

van der Waals' equation becomes :

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

or $$p(V - b) = RT$$

$$pV - pb = RT$$

$\therefore$ $$pV = RT + pb$$

D6. (*c*) : $\frac{r_X}{r_Y} = \frac{V_X}{V_Y}$ for the same time period, *t*

Also, $$\frac{r_X}{r_Y} = \sqrt{\frac{M_Y}{M_X}}$$

$$\frac{d}{24 - d} = \sqrt{\frac{40}{10}} = 2$$

or $$d = 48 - 2d$$

$\therefore$ $$3d = 48$$

$\therefore$ $$d = \frac{48}{3} = 16 \text{ cm}$$

D7. (*d*) : As the collision frequency increases, molecular speed decreases.

Integer Type Questions

1. (4) Gas X : r.m.s. = $\sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times R \times 400}{40}}$

Gas Y : Most probable speed

$$= \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \times R \times 60}{M}}$$

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As r.m.s. of gas X = Most probable speed of gas Y

$$\sqrt{\frac{3\times R\times 400}{40}} = \sqrt{\frac{2\times R\times 60}{M}}$$

or $$\frac{3\times R\times 400}{40} = \frac{2\times R\times 60}{M}$$

$$\therefore \quad M = \frac{2\times 60\times 40}{3\times 400} = 4$$

2. (5) $$pV = nRT \quad \text{or} \quad T = \frac{pV}{nR}$$

$$= \frac{3.32\times 5}{4.0\times 0.083} = 50 \text{ or } 5\times 10 \text{ K}$$

3. (2) $r \propto \sqrt{T}$ $\therefore$ $$\frac{r_1}{r_2} = \sqrt{\frac{T_1}{T_2}} = \sqrt{\frac{300 \text{ K}}{1200 \text{ K}}} = \frac{1}{2}$$

$$\therefore \quad r_2 = 2r_1$$

4. (4) $$p_A V = \frac{W_A}{M_A} RT$$

$$2 \text{ bar} \times V = \frac{1}{M_A} RT \qquad ...(i)$$

After addition of 2g of gas B

$$3 \text{ bar} \times V = \left(\frac{1g}{M_A} + \frac{2g}{M_B}\right) RT \qquad ...(ii)$$

From (ii) and (i)

$$\frac{3}{2} = \frac{\left(\frac{1}{M_A} + \frac{2}{M_B}\right)}{\left(\frac{1}{M_A}\right)}$$

$$= \frac{\frac{M_B + 2M_A}{M_A . M_B}}{\frac{1}{M_A}} = \frac{M_B + 2M_A}{M_B} = 1 + \frac{2M_A}{M_B}$$

or $$\frac{2M_A}{M_B} = \frac{3}{2} - 1 = \frac{1}{2}$$

or $$\frac{M_A}{M_B} = \frac{1}{4}$$

or $$M_B = 4\, M_A$$

6. (3) Since volume remains constant,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{P_1}{300 \text{ K}} = \frac{P_2}{900 \text{ K}} \quad \text{or} \quad P_2 = 3P_1$$

8. (4) Universal gas constant, $R = k_B \times N_A$ where k_B is the Boltzman constant and N_A is the Avogadro's number. The values of both k_B and N_A contain four significant figures. Therefore, the value of R must contain four significant figures.

9. (4) Diffusion coefficient $\propto \lambda \times C_{mean}$

Mean free path; $\lambda \propto \frac{T}{p}$

Mean speed, $C_{mean} \propto \sqrt{T}$

Diffusion coefficient $\propto \frac{T}{p} \times \sqrt{T}$

$$\propto \frac{T^{3/2}}{p}$$

$$= K\frac{T^{3/2}}{p}$$

At temperature T_1 and pressure p_1

$$D_1 = \frac{K(T_1)^{3/2}}{p_1}$$

If T_1 is increased 4 times and pressure in increased 2 times,

$$D_2 = \frac{K(4T_1)^{3/2}}{2p_1}$$

$$\frac{D_2}{D_1} = \frac{(4)^{3/2}}{2} = \frac{2^3}{2} = 4$$

NCERT Exemplar Problems: MCQs Type-I

1. (c) At high altitudes, pressure is low. Hence, boiling takes place at lower temperature and therefore, cooking takes more time. In pressure cooker, pressure is high and hence boiling point increases.

3. (c) At a particular temperature pV = constant. Thus,
$p_1V_1 = p_2V_2 = p_3V_3 = p_4V_4$.
As $V_1 > V_2 > V_3 > V_4$, therefore, $p_1 < p_2 < p_3 < p_4$.

4. (c) Greater the polarizability of the interacting particles, greater is the magnitude of the interaction energy.

6. (c) Partial pressure of O_2 =
Mole fraction of O_2 × Total pressure of mixture
$= \frac{4}{8}\times 1 = 0.8 \text{ atm} = 0.8 \times 10^5 \text{ Nm}^{-2}$
or $= 8 \times 10^4 \text{ Nm}^{-2}$.

7. (a) At constant volume, as the temperature is increased, pressure also increases.

8. (d) Higher the critical temperature, more easily is the gas liquefied. Hence order of liquefication : O_2, N_2, H_2, He.

10. (a) Lower the atmospheric pressure, lower is the boiling point because a liquid boils when vapour pressure above it becomes equal to atmospheric pressure.

11. (a) For ideal gas, pV = constant at all pressures.

12. (c) With increase of temperature, kinetic energy increases. Hence, forces of attraction are more easily overcome and therefore, viscosity decreases.

NCERT Exemplar Problems: MCQs Type-II

14. (b, c) : In a gaseous state, there is a complete disorder of molecules as there is random motion of molecules.

15. (a, d) : 1 mole of dioxygen at STP = 32 g = 22.4 L.

17. (b, d) : Vapour pressure does not depend upon the quantity of water or size of the vessel. It decreases on adding salt to water or decreasing the temperature of water.

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Unit Practice Test

for Board Examination

Time Allowed : 1 Hr. ***Maximum Marks : 25***

1. Define Dalton's law of partial pressures.	(1)
2. CO_2 is heavier than N_2 and O_2 gases present in the air but it does not form the lower layer of the atmosphere. Why?	(1)
3. What is the significance of the van der Waals constants?	(1)
4. What is the effect of temperature on : (*i*) viscosity and (*ii*) surface tension.	(1)
5. Why are the gases H_2 and He not liquefied at room temperature by applying very high pressure?	(1)
6. Density of a gas is found to be 5.46 g dm^{-3} at 27°C and 2 bar pressure. What will be its density at N.T.P.?	(2)
7. 2.49 g of a gas at 95°C occupied the same volume as 0.184 g of dihydrogen at 17°C, at the same pressure. What is the molar mass of the gas?	(2)
8. What are the two faulty assumptions in the kinetic molecular theory of gases which are responsible for the deviation of ideal behaviour of gases ?	(2)
9. A drain cleaner contains small bits of Al which react with caustic soda to produce H_2 gas. What volume of H_2 at 20°C and 1 bar pressure will be released when 0.15 g of Al reacts?	(3)
10. (*a*) How is molar mass of an ideal gas calculated from ideal gas equation? (*b*) What is the kinetic energy of 4 g of oxygen at –13°C	(3)
11. What is meant by liquefication of gases. Explain briefly Andrews isotherms for carbon dioxide.	(3)
12. (*a*) What is meant by compressibility factor of a gas? Is it always equal to or greater than 1 for all gases ? (*b*) 1 mole of SO_2 occupies a volume of 320 mL at 27°C and 4×10^6 Pa pressure. Calculate the compressibility factor of the gas. (2 + 3)	(5)

▶ To check your performance, see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part I of the book.

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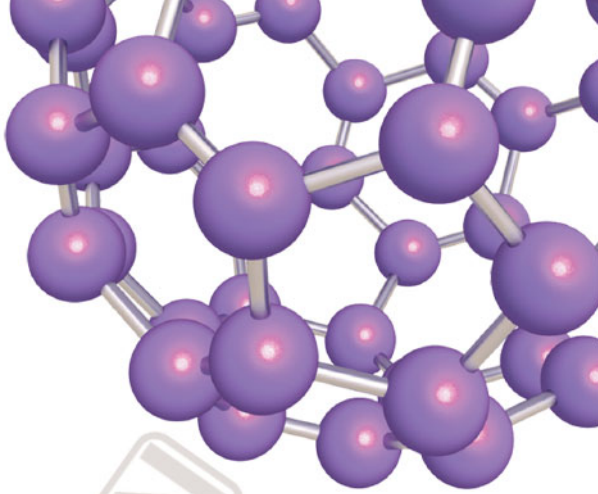
SOLID STATES



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SOLID STATE OF MATTER

The properties of the solids not only depend upon the nature of the constituents but also on their arrangements and the types of forces which hold the constituent particles together in a tightly packed arrangement.

GENERAL CHARACTERISTICS OF SOLID STATE

Some of the important **characteristic properties** of solids are :

(*i*) Solids have definite mass, volume and shape.

(*ii*) The intermolecular distances in solids are short and intermolecular forces are strong.

(*iii*) The constituent particles (atoms, ions or molecules) of solids have fixed positions and can only oscillate about their mean positions.

(*iv*) Solids are almost incompressible and rigid.

(*v*) The density of solids is greater than that of liquids and gases.

(*vi*) Solids diffuse very slowly as compared to liquids and gases.

(*vii*) Most solids become liquids when heated. This process is known as **melting** and the temperature at which a solid changes into a liquid is called the **melting point**. The melting point of a solid depends upon the nature of the solid and melting points of solids vary widely.

CLASSIFICATION OF SOLIDS

Solids can be classified on the basis of nature of order present in the arrangement of constituent particles (atoms, ions or molecules) into two types as:

1. Crystalline solids
2. Amorphous solids

1. Crystalline solids

The substances whose constituent particles (atoms, ions or molecules) are arranged in a definite geometric pattern in three dimensional space *are called* **crystalline solids.**

X-ray diffraction studies of crystalline solids reveal that in these solids, the constituents (atoms, ions or molecules) are arranged in a definite orderly arrangement. The regular arrangement of the constituents extends throughout the three dimensional network of crystals. In other words, the crystalline substances are said to have **long range order**. This means that in crystalline solids, there is a regular pattern or arrangement of particles which repeats itself periodically over the entire crystal. In fact, a crystalline solid consists of a large number of small crystals, each of them having a definite characteristic geometrical shape.

Most of the substances (elements and compounds) form crystalline solids. For example, the elements like copper, silver, iron, sulphur, phosphorus and iodine and common compounds such as sodium chloride, potassium nitrate, zinc sulphide, quartz, etc. all form crystalline solids.

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2. Amorphous solids

The substances whose constituent particles are not arranged in any regular arrangement *are called* **amorphous solids** (Greek *amorphos* meaning no form).

The amorphous solids have a random, disordered arrangement of constituents. Therefore, they do not have definite shape or form like crystalline solids. It is observed that some amorphous solids have some orderly arrangement but it is not extended to more than a few Angstrom units. Thus, the amorphous solids are said to have **short range order.** This means that in amorphous solids, a regular and periodically repeating pattern is observed over short distances only. These regular patterns are scattered and in between, the arrangement is disordered.

The common examples of amorphous solids are glass, rubber, plastic, coal, etc.

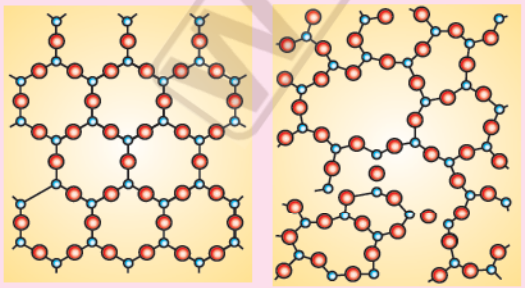
Differences between Crystalline and Amorphous solids

The important differences between crystalline and amorphous solids are :

1. Characteristic geometry. *The crystalline solids have definite regular geometry because of orderly arrangement of constituents (atoms, molecules or ions) in three dimensional space.* On the other hand, amorphous solids do not possess any regular arrangement of constituent particles and therefore, do not have any definite geometric shape.

Structure of quartz (crystalline) and quartz glass (amorphous)

Quartz is a form of SiO_2 (silica). It has tetrahedral SiO_4 units which are orderly arranged in crystalline quartz as shown in Fig. 1 (*a*). In this arrangement, SiO_4 tetrahedra are connected to one another such that oxygen atom of each SiO_4 tetrahedral is shared with another atom. When SiO_2 is melted and the melt is cooled, it forms quartz glass which is amorphous. In this state, the SiO_4 units are randomly joined [Fig 1 (*b*)]. Thus, in quartz (crystalline), SiO_4 units are orderly arranged while in quartz glass (amorphous), the SiO_4 units are randomly arranged. While the two structures are almost identical, yet in case of amorphous quartz glass, there is no long range order. The structure of amorphous solids is similar to that of liquids.



(*a*) Crystalline quartz (*b*) Amorphous quartz glass

Fig.1. Two dimensional structure of (*a*) crystalline quartz and (*b*) quartz glass.

2. Melting points. *The crystalline solids have sharp melting points.* On the other hand, amorphous solids do not have sharp melting points. Therefore, crystalline solids have definite enthalpies of fusion whereas amorphous solids do not have definite enthalpies of fusion. The amorphous solids, in fact, on heating first soften and then melt over a range of temperature. Therefore, amorphous solids can be moulded and blown into various shapes. For example, when glass is heated gradually, it softens and starts to flow without undergoing a definite and abrupt change into liquid state. Therefore, glass can be moulded and given any desired shape.

It has been observed that on heating and then cooling slowly (*i.e.*, annealing) some amorphous solids become crystalline at some temperature. It is for this reason that **some glass objects from ancient civilizations are found to become milky in appearance.** Milkiness of glass is due to the fact that it undergoes heating during the day and cooling at night (i.e., annealing) over a number of years. As a result, it acquires some crystalline character.

R U Curious...

❑ ***Glass window panes of very old buildings are found to be slightly thicker at the bottom than at the top.***

‣ Glass is an amorphous solid which is super cooled liquid of very high viscosity and behaves more or less like a liquid. The glass flows down very slowly and hence makes the bottom portion slightly thicker.

3. Isotropy and anisotropy. In crystalline substances, some of the physical properties such as electrical conductivity or refractive index have different values when measured along different directions in the same crystals. **Such substances which have physical properties different in different directions** are called **anisotropic.** Thus, *crystalline substances are anisotropic.*

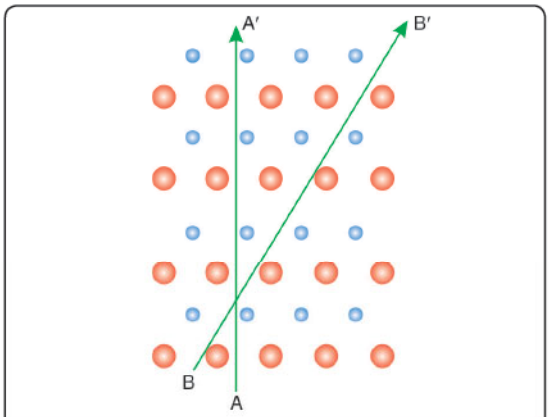


Fig. 2. Anistropy in crystalline substances.

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On the other hand, **amorphous substances have physical properties same in all directions** and are called **isotropic.** For example, the velocity of light passing through a crystal varies with the direction in which it is measured. Thus, anisotropy is a strong evidence for the existence of orderly arrangement in crystalline solids. This is shown in Fig 2. In this figure, a simple two dimensional arrangement of two different kinds of atoms is shown. It is clear from the figure that if the properties are measured along two different directions AA′ and BB′, different types of particles come on the way. Along AA′ direction only one type of particles come on the way while along BB′ direction, alternate types of particles come on the way. Hence, the crystalline solids have different physical properties in different directions. In amorphous solids, the constituent particles are arranged at random and in disorderly manner and therefore, all directions are identical and all properties are same in all directions.

4. Cleavage. *Crystalline solids can be cleaved along definite planes.*When cut with a sharp edged tool *(e.g.* knife) they split into two pieces and the newly generated surfaces are plain and smooth. On the other hand, amorphous solids cannot be cleaved along definite planes. When cut with a sharp edged tool (*e.g.*, knife) they undergo irregular breakage and split into two pieces with irregular surfaces. This is shown in Fig 3.

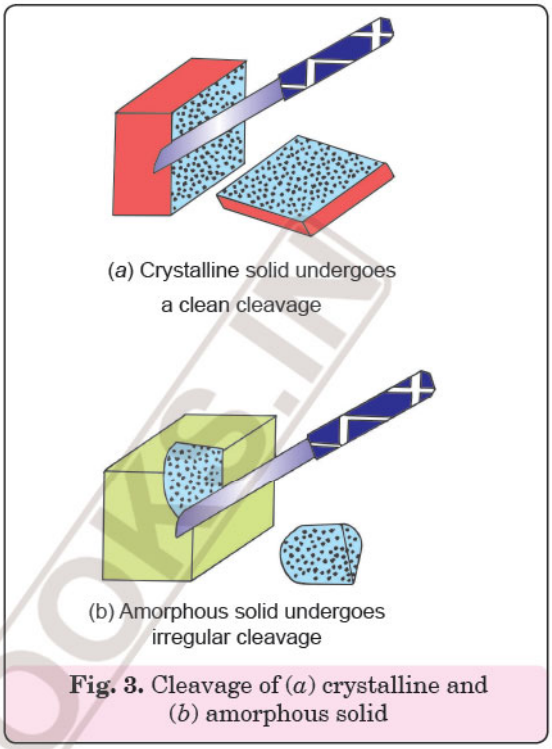

Fig. 3. Cleavage of (*a*) crystalline and (*b*) amorphous solid

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Pseudo solids or Super cooled liquids

Like liquids, amorphous solids have a tendency to flow. Therefore, sometimes these are also called **pseudo solids** or **super cooled liquids.** Glass is a common example of pseudo solid. It softens on heating to a certain temperature. It behaves more or less like a fluid. Pitch is another example of pseudo solid.

Thus, the pseudo solids possess the following characteristics:

(*i*) They do not have sharp melting point but soften over a range of temperature.
(*ii*) They can be easily distorted by applying force.
(*iii*) They can flow slowly under their own weight and lose shape.

The important differences between crystalline solids and amorphous solids are summed up below :

Table 1. Distinction between crystalline and amorphous solids.

Property	Crystalline solids	Amorphous solids
1. Shape	The crystalline solids have definite characteristic shape.	The amorphous solids have irregular shapes.
2. Order in arrangement of constituent particles.	They have regular arrangement of the constituent particles. They are said to exhibit long range order.	They donot have any regular arrangement of the constituent particles. They may have short range order.
3. Melting point	They have sharp and characteristic melting point.	They donot have sharp melting point. They gradually soften over a range of temperature.
4. Enthalpy of fusion	They have a definite and characteristic enthalpy of fusion.	They donot have definite enthalpy of fusion.
5. Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth.	When cut with a sharp edged tool they cut into two pieces with irregular surfaces.
6. Anisotropy	They are anisotropic and have different physical properties in different directions.	They are isotropic and have same physical properties in all directions.
7. Nature	They are true solids	They are pseudo solids and supercooled liquids.
Common examples	Copper, silver, iron, common salt, zinc suphide, potassium nitrate, etc.	Glass, rubber, plastics, etc.

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REMEMBER

- The substances which show same physical properties (electrical conductivity, thermal conductivity, refractive index, etc.) in all directions are called **isotropic substances**.
- The substances which show different physical properties (electrical conductivity, thermal conductivity, refractive index, etc.) in different directions are called **anisotropic substances**.

⇒ **Crystalline substances exhibit anisotropy while amorphous substances exhibit isotropy.**

⇒ **Liquids and gases are also isotropic.**

Uses of Amorphous Solids

Amorphous solids such as glass, rubber, plastic, etc. find many uses in our daily lives because of their unique characteristics. For example,

(*i*) The most widely used amorphous solids are *inorganic glasses* which are used in construction, houseware, laboratoryware, etc.

(*ii*) Amorphous silicon is the best photovoltaic material for converting the sunlight into electricity (in photovoltaic cells).

(*iii*) Rubber is also an amorphous solid which is used in making tyres, shoe soles, etc.

(*iv*) A large number of plastics which are amorphous solids are used in making articles of daily use.

CLASSIFICATION OF CRYSTALLINE SOLIDS

The crystalline solids can be classified into following four types depending upon the nature of intermolecular forces operating in them.

1. Molecular solids *2. Ionic solids*
3. Metallic solids *4. Covalent or network solids*

1. Molecular solids

These are crystalline substances in which the constituent particles are molecules. The molecules are held together by dispersion forces or London forces, dipole-dipole forces or hydrogen bonds. These are further subdivided into the following categories :

(*a*) Non-polar molecular solids. *These are those crystalline substances in which the constituent particles are either atoms like those of noble gases (helium, neon, argon, etc.) or non-polar molecules.* For example, solid helium, solid argon, solid hydrogen, solid carbon dioxide, iodine, etc. In these solids, the atoms or molecules are held by weak dispersion forces or London forces.

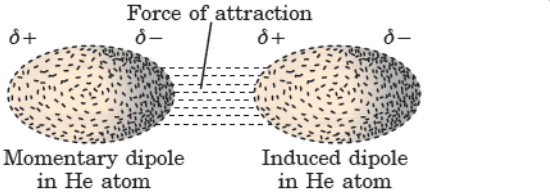

Fig. 4. Weak dispersion or London forces in solid He

These solids have the following characteristics:

(*i*) They are generally soft.

(*ii*) They have low melting points.

(*iii*) They are usually in liquid or gaseous state at room temperature and pressure.

(*iv*) They are non-conductors of electricity because they consist of neutral molecules in solid as well as in dissolved state.

(*b*) Polar molecular solids. *These comprise of molecules of substances formed by polar covalent bonds.* For example, solid HCl, solid SO_2, solid NH_3, etc. The molecules in such solids are held together by relatively stronger dipole - dipole forces.

Fig. 5. Dipole – dipole forces in solid HCl

They have characteristics similar to non-polar covalent molecules as given below :

(*i*) These solids are also soft.

(*ii*) They are non-conductors of electricity.

(*iii*) They have low melting and boiling points. But their melting and boiling points are higher than those of non-polar molecular solids.

(*iv*) Because their melting and boiling points are not very high, most of these are gases or liquids under room temperature and pressure conditions.

(*c*) Hydrogen bonded molecular solids. *The molecules of such solids contain hydrogen bonds between them.* For example, in case of solid water (ice), the negative end of one molecule ($O^{\delta-}$) attracts the positive end of a neighbouring molecule ($H^{\delta+}$) forming hydrogen bond between O and H. These solids contain hydrogen bonds between H and highly electronegative elements; F, O or N. These solids have the following characteristics :

(*i*) They are generally volatile liquids or soft solids under room temperature and normal pressure conditions.

(*ii*) They are non-conductors of electricity.

(*iii*) Their melting and boiling points are generally higher than those of non polar molecular solids and polar molecular solids.

2. Ionic Solids

Ionic solids consist of positively and negatively charged ions arranged in a regular manner throughout the solid. The ions are held together by strong coulombic (or electrostatic) forces. Thus, in ionic solids, the constituent particles are **ions.**

The regular arrangement of ions extends continuously throughout the crystal. For example, in sodium chloride, Na^+ and Cl^- ions have a definite

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regular arrangement as shown in Fig. 6. In this arrangement, each Na^+ is surrounded by six Cl^- ions and each Cl^- is surrounded by six Na^+ ions.

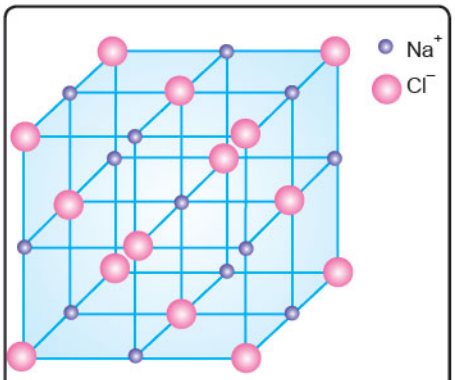

Fig. 6. Structure of sodium chloride.

Similar regular arrangements are also observed in other ionic solids. The main characteristics of ionic crystals are :

(*i*) Ionic solids are very hard and brittle.

(*ii*) They have very high melting and boiling points.

(*iii*) They are poor conductors of electricity and, therefore, are insulators in solid state. This is because in the solid state, the ions are not free to move about. However, in the molten state or when dissolved in water (aqueous solution), the ions become free to move about and they conduct electricity.

(*iv*) They have high enthalpies of vaporisation.

(*v*) Ionic crystals are soluble in water and also in other polar solvents. They are insoluble or very slightly soluble in non-polar solvents such as benzene, carbon tetrachloride, carbon disulphide.

The common examples of ionic crystals are : salts like NaCl, KNO_3, LiF, Na_2SO_4, etc.

3. Metallic solids or crystals

In metallic crystals, the constituent particles are positive ions (called kernels) immersed in a sea of mobile electrons. This is shown in Fig. 7.

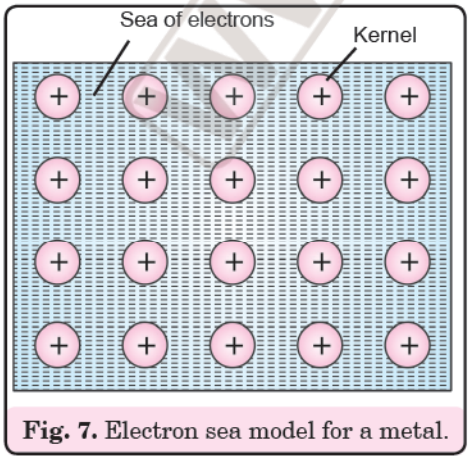

Fig. 7. Electron sea model for a metal.

The electrons in metallic crystals are mobile and are evenly spread throughout the crystal. Each metal atom contributes one or more electrons towards this sea of mobile electrons. These free mobile electrons are responsible for high electrical and thermal conductivities of metals. When electric field is applied, these electrons flow through the network of positive ions (called *kernels*). Similarly, when heat is supplied to one portion of a metal, the thermal energy is uniformly spread throughout the crystal by free electrons. **The forces present between the metal ions** are **metallic bonds**. The main characteristics of metallic crystals are :

(*i*) Metallic crystals may be hard as well as soft.

(*ii*) They are good conductors of heat and electricity.

(*iii*) They have metallic lustre and colour in certain cases.

(*iv*) They are malleable and ductile. Due to malleable nature, they can be beaten into sheets and drawn into wires.

(*v*) They have moderate enthalpies of fusion.

The examples of metallic crystals are **common metals such as nickel, copper and alloys.**

4. Covalent or network solids or crystals

In covalent crystals, the constituent particles are non-metal atoms which are linked to the adjacent atoms by covalent bonds throughout the ***crystal.*** In other words, there is a continuous network of covalent bonds forming a giant three dimensional structure. They are also called **giant molecules.** Covalent bonds are strong and directional in nature and therefore, atoms in these solids are held very strongly at their positions. The important characteristics of covalent crystals are :

(*i*) The covalent crystals are hard.

(*ii*) They have extremely high melting points and may even decompose before melting.

(*iii*) They are poor conductors of electricity and are insulators.

The common examples of covalent crystals are : diamond, carborundum (silicon carbide), quartz (SiO_2), boron nitride (BN), etc.

Diamond is a typical example of covalent crystal. It has a network structure consisting of a very large number of carbon atoms bonded to each other. Each carbon atom is bonded to four other carbon atoms by single covalent bonds. It is clear from Fig. 8 *(a)*, that each carbon atom lies at the centre of a regular tetrahedron and the other four carbon atoms are present at the corners of the tetrahedron. Therefore, there is a three dimensional network of strong covalent bonds. *This makes diamond an extremely hard crystal with very high melting point (3843 K).* Since all the valence electrons of carbon are strongly held in carbon-carbon bonds, *diamond is a poor conductor of electricity.*

Graphite is also a covalent solid but it is *soft and a good conductor of electricity.* Its **exceptional**

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properties are due to its typical structure as shown in Fig. 8 (*b*).

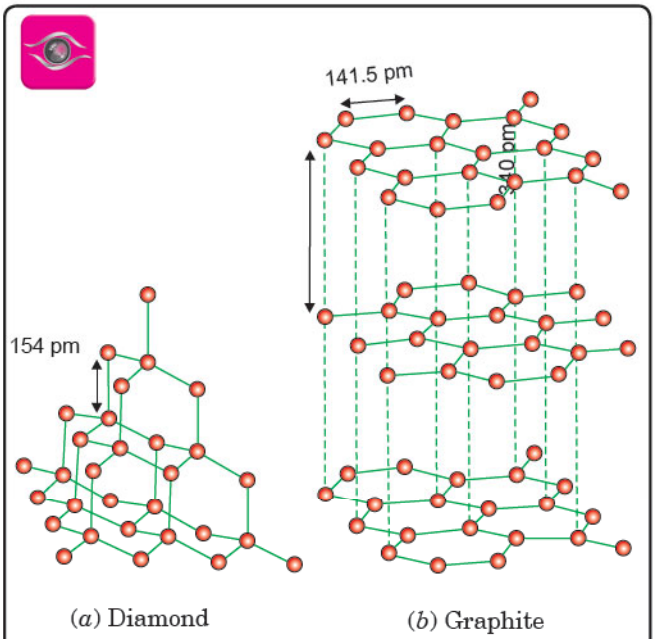

Fig. 8. Structure of (*a*) diamond and (*b*) graphite

In graphite, carbon atoms are arranged in different layers consisting of hexagonal rings. In these layers, each carbon atom is covalently bonded to three other neighbouring carbon atoms by single covalent bonds in the same layer. The fourth valence electron of each carbon atom is present between different layers and is free to move about. Because of the presence of free electrons, *graphite is a good conductor of electricity.* Further, the different layers are separated by a large distance (340 pm), which is greater than carbon-carbon bond length. This suggests that only weak van der Waals forces are present between these layers and therefore, these layers can slide one over the other. This makes *graphite a soft solid and a good solid lubricant.*

Learning Plus

- In **diamond,** each carbon atom is sp^3 **hybridised.**
- In **graphite,** each carbon atom is sp^2 **hybridised.**

R U Curious...

- ***Graphite is a good conductor of electricity, though it is a non-metal.***

❑ Graphite is a covalent solid but it is soft and a good conductor of electricity. Its exceptional behaviour is because of its typical structure having π-delocalised electrons in hexagonal rings which are free to move.

The main characteristics of various types of crystals are summed up in Table 2.

Table 2. Summary of the characteristics of various types of solids

Type of Solid	Constituent particles	Bonding/ attractive forces	Examples	Physical properties			
				Physical nature	Melting point	Approx binding energy (kJ mol^{-1})	Electrical conductivity
1. Molecular	Small covalent molecules					Less than 40	Insulators
(i) Non-polar	Non polar molecules or atoms of noble gases	Dispersion or London forces	Solid CO_2, argon, H_2, I_2, CCl_4, CH_4	Soft	Very low		
(ii) Polar	Polar molecules	Dipole- dipole interactions	HCl, SO_2	Soft	Low		
(iii) Hydrogen bonded	Molecules containing H bonded to F, O or N	Hydrogen bonding	Ice (H_2O)	Hard	Low		
2. Ionic solids	Positive and negative ions $BaSO_4$, LiF	Strong electrostatic or coulombic forces	NaCl, MgO, BaO, CaF_2, ZnS, KCl,	Hard but brittle	Very high (~ 1500K)	400–4000	Insulators in solid state but conductors in molten state and in aqueous solution.
3. Metallic solids	Positive ions in a sea of delocalized electrons	Metallic bonding [electric attraction between kernels (positive ions) and electrons]	Common metals (Cu, Ag, Fe, Mg) and some alloys	Hard but malleable and ductile	Moderate to high m pt. (800–1000 K)	70–1000	Good conductors of heat and electricity
4. Covalent or network solids	Atoms	Covalent (electron sharing) bonding	Quartz (SiO_2) SiC, diamond (C) AlN graphite (C)	Hard Soft	Very high (~ 4000K)	150–500	Insulators (except graphite which is conductor)

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- It may be noted that some substances adopt different structural arrangements under different conditions. Such arrangements are called **polymorphs** (meaning *many forms*). For example, diamond and graphite are two different polymorphic forms of carbon.

  Polymorphic forms are also called **allotropes**. These different structures have different properties such as melting point, density, etc. For example, as we know, graphite is soft and a good conductor of electricity while diamond is hard and a poor conductor of electricity.

Isomorphism and Polymorphism

- The existence of two or more crystalline solids having similar chemical composition in the same crystalline form or structure is called isomorphism (*iso*–same, *morphous*–form). For example, Na_3PO_4 and Na_3AsO_4 are isomorphs.
- The existence of a particular substance in more than one crystalline forms is called **polymorphism.** For example, calcium carbonate exists in two crystalline forms known as **calcite** and **aragonite.**

❑ In case of elements, polymorphism is also called **allotropy.**

SOLVED EXAMPLES

❑ **Example 1.**

Classify the following as amorphous or crystalline solids :

(i) Naphthalene (ii) Teflon (iii) Polyurethane (iv) Benzoic acid (v) Potassium nitrate (vi) Cellophane (vii) Polyvinyl chloride (viii) Fibre glass (ix) Copper (x) Zinc sulphide **N.C.E.R.T.**

Solution :

Amorphous solids : (*ii*) Teflon (*iii*) Polyurethane (*vi*) Cellophane (*vii*) Polyvinyl chloride (*viii*) Fibre glass

Crystalline solids : (*i*) Naphthalene (*iv*) Benzoic acid (*v*) Potassium nitrate (*ix*) Copper (*x*) Zinc sulphide.

❑ **Example 2.**

Classify the following solids as ionic, metallic, molecular, network (covalent) or amorphous :

(i) Tetraphosphorus decaoxide (P_4O_{10}) (ii) Graphite (iii) SiC (iv) Brass (v) Rubidium (vi) I_2 (vii) Ammonium phosphate, $(NH_4)_3PO_4$ (viii) LiBr (ix) Si (x) Plastics (xi) P_4 (xii) Solid CO_2. **N.C.E.R.T.**

Solution : The solids are classified as :

Ionic : $(NH_4)_3PO_4$, LiBr

Metallic : Brass, Rubidium

Molecular : P_4O_{10}, I_2, P_4, solid CO_2

Network (covalent) : Graphite, SiC, Si

Amorphous : Plastics.

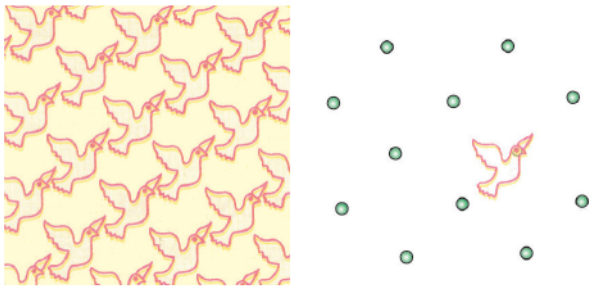
CRYSTAL LATTICE OR SPACE LATTICE AND UNIT CELL

The crystalline solids have definite orderly arrangement of their constituent particles in three dimensions. The positions of these particles in a crystal, relative to one another, are usually shown by points. The arrangement of an infinite set of these points is called **space lattice.** The positions which are occupied by the atoms, ions or molecules in the crystal lattice are called **lattice points** or **lattice sites.**

To understand space lattice, let us first learn about two dimensional lattices and then three dimensional lattices.

A. Two Dimensional Lattices

A **two dimensional lattice** *is a regular arrangement of constituent particles (atoms, ions or molecules) in a plane.* A two dimensional pattern is shown in Fig. 9 (*a*) and the lattice is shown by points in Fig. 9 (*b*).



(*a*) Pattern (*b*) Lattice points

Fig. 9. Two dimensional pattern

There are **five types of two dimensional lattices.** These are, square, rectangular, parallelogram, rhombic and hexagonal lattice as shown in Fig. 10 ahead. These differ in symmetry of the arrangement of points. *The hexagonal lattice has the most symmetrical arrangement of points while parallelogram lattice has the least symmetrical arrangement* of points.

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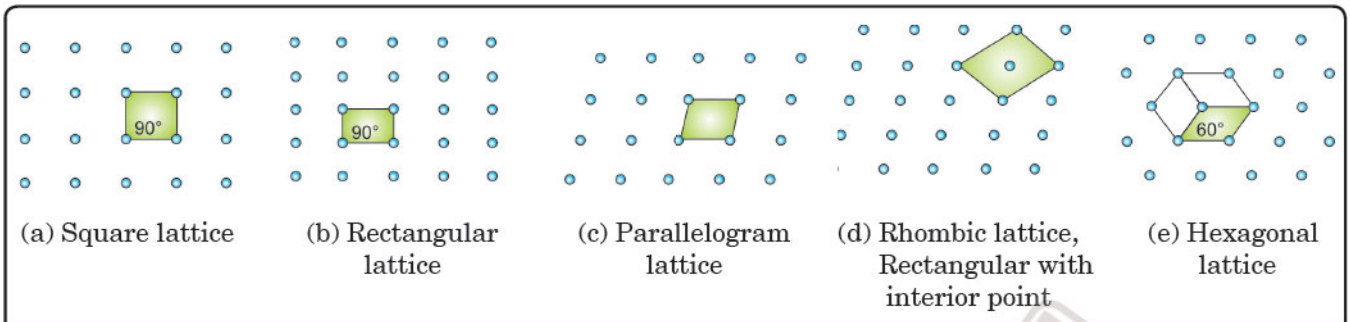

Fig. 10. Five different two dimensional lattices.

Because of the regular repeating arrangement of the points in a two dimensional lattice, we need only to describe a small part of the lattice (called **motif**) in order to specify it completely. For example, we select four points in two dimensional lattice and connect them to give a parallelogram. This smallest part is known as **unit cell.** We can generate the complete lattice by repeatedly moving the unit cell in the direction of its edges by a distance equal to the cell edge as shown in Fig. 11.

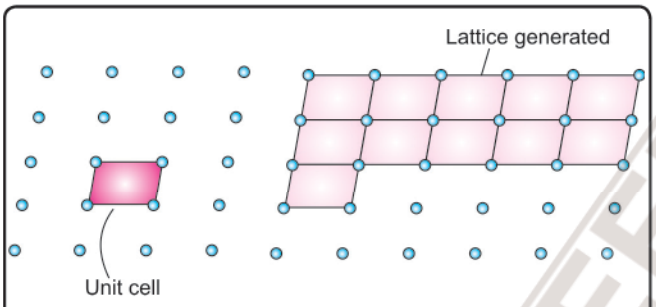

Fig. 11. (*a*) A unit cell (*b*) The complete lattice generated by repeatedly moving the unit cell in the direction of its cell edges by distance equal to cell edge.

Thus, **the unit cell gives the shape of the entire lattice.** However, it may be noted that for any given lattice, the unit cells may be chosen in many different ways. This is because a lattice contains a very large number of atoms and numerous identical points may be found. Naturally, a question arises. "What are the characteristics of this unit cell?" The most convenient cell is the smallest unit cell which has the full symmetry of the lattice. For the square, rectangular and parallelogram lattices, the unit cells chosen are the square, the rectangle and the parallelogram respectively. However, for the hexagonal lattice the unit cell is a rhombus with an angle of 60°.

For the rhombic lattices, a rectangular unit cell with an interior point is generally selected. A cell with an interior point is called a **centered unit cell.** The unit cells which do not contain any interior point are called **primitive unit cells.**

Thus, we see that for describing a two dimensional lattice, we must specify the unit cell by the lengths of the edges and the angles between them.

Thus, the five two dimensional lattices and their unit cells are :

Two dimensional lattice	Unit cell
(*a*) Square lattice	Square
(*b*) Rectangular lattice	Rectangle
(*c*) Parallelogram lattice	Parallelogram
(*d*) Rhombic lattice	Rectangular with an interior point
(*e*) Hexagonal lattice	Rhombus with an angle of 60°

B. Three Dimensional Crystal Lattice

The crystalline solids have definite three dimensional arrangement of constituent particles (atoms, ions or molecules). If the three dimensional arrangement of constituent particles in a crystal is represented diagrammatically by depicting each particle by a point, the arrangement is called crystal lattice or space lattice. Thus, **a crystal lattice** is a

regular arrangement of the constituent particles (atoms, ions or molecules) of a crystalline solid in three dimensional space.

A three dimensional crystal lattice is shown in Fig. 12.

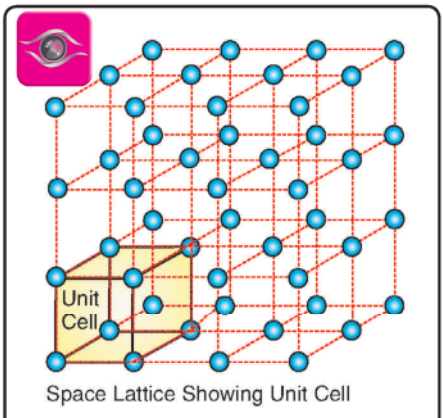

Fig. 12. Three dimensional lattice.

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Like two dimensional lattice, if we carefully look a crystal lattice, it is observed that we can select a group of lattice points (a smallest three dimensional portion) which is repeated over and over again in the whole crystal lattice. This smallest repeating pattern (motif) is called the unit cell. Thus, a **unit cell** may be defined as :

the smallest three dimensional repeating portion of a space lattice which when repeated over and again in different directions produces the complete crystal lattice.

This smallest repeating pattern (unit cell) represents the shape of the entire crystal. We can generate the complete lattice by repeatedly moving the unit cell in the direction of its edges by a distance equal to the cell edge. In fact, the crystal may be considered to consist of an infinite number of unit cells. The unit cell in the above crystal lattice is shown by solid lines.

Parameters of a Unit cell

A unit cell is characterized by

(*i*) its dimensions (lengths) along the three edges as a, b and c. These edges may or may not be mutually perpendicular.

(*ii*) angles α, β and γ between the pair of edges. The angle α is between the edges b and c, angle β is between the edges c and a and angle γ is between the edges a and b. Thus, a unit cell is characterized by six parameters, a, b, c, α, β and γ. The parameters of a unit cell are shown in Fig. 13. The complete crystal lattice can be obtained by extending the unit cell in all the three directions.

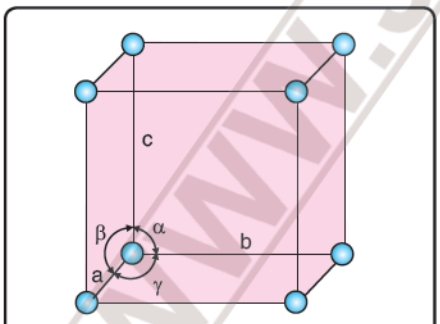

Fig. 13. Parameters of a unit cell.

Characteristics of a Crystal Lattice

Let us sum up the characteristics of a crystal lattice. The following are the characteristics of a crystal lattice.

(*i*) Each point in a crystal lattice is called lattice point or lattice site.

(*ii*) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.

(*iii*) The three dimensional arrangement of lattice points represents a crystal lattice.

(*iv*) Lattice points are joined by straight lines to bring out the geometry of the lattice.

Types of Unit Cells

There are basically two types of unit cells constituting different crystal systems. These are :

(*i*) *Primitive or simple unit cells*

(*ii*) *Non primitive or centred unit cells.*

(*i*) Primitive unit cells. *These are unit cells which have points (or particles) only at the corners.* These are also called **simple unit cells**.

(*ii*) Non-primitive *or* centred unit cells. *These are unit cells which have points (or particles) at the corners as well as at some other positions.*

The centred unit cells are of three types :

(*a*) **Face centred unit cells** *in which the points are present at the corners as well as at the centre of each face.*

(*b*) **Body centred unit cells** *in which the points are present at all the corners as well as at the body centre of the unit cell.*

(*c*) **End centred unit cells** *in which the points are present at all the corners and at the centre of two opposite faces.*

Seven Crystal Systems

When a unit cell in a crystal lattice has lattice points only at its corners it is called a **simple** or **primitive unit cell.** In all, there are **seven types** of *simple or primitive* unit cells among crystals. These unit cells are characterised by the axial lengths a, b and c and the angles α, β and γ. These are called **seven crystal systems** or **crystal habits.** These are shown in Fig. 14. All crystals can be placed in one of these seven crystal systems. These are :

1. Cubic. All the three axes are of equal length and are at right angles to each other ($a = b = c$, all angles = 90°).

2. Tetragonal. The three axes are at right angles to each other but only the two axes are equal ($a = b \neq c$, all angles = 90°).

3. Orthorhombic. It has three unequal axes which are at right angles to each other ($a \neq b \neq c$, all angles = 90°).

4. Monoclinic. The three axes are of unequal length and two angles are of 90° ($a \neq b \neq c$, two angles = 90° and one angle ≠ 90°).

5. Hexagonal. It has two edges of equal length ($a = b$) and two angles of 90° and one angle of 120° ($a = b \neq c$, two angles of 90° and one angle of 120°).

6. Rhombohedral or trigonal. The three axes are of equal length which are inclined at the same angle but the angle is not equal to 90° ($a = b = c$, all three angles equal but not equal to 90°).

7. Triclinic. The three axes are of unequal length, and all angles are different but none is perpendicular to any of the others ($a \neq b \neq c$, all angles different and none equal to 90°).

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These seven crystal systems are shown in Fig. 14 and are summed up in Table 3.

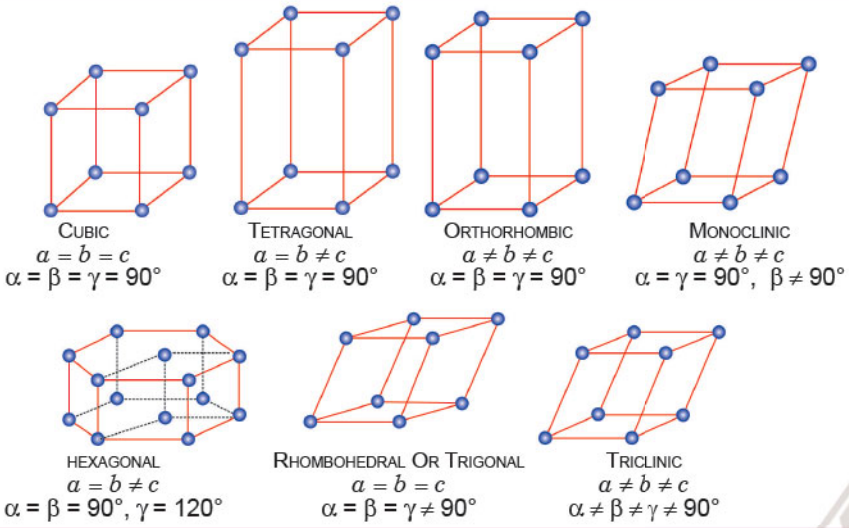


Fig. 14. The seven crystal systems.

REMEMBER

It may be noted that among the seven crystal systems :

⇒ **Cubic is the most symmetrical while**

⇒ **Triclinic is the most unsymmetrical system**

The characteristics of the seven crystal systems are summed up in Table 3.

Table 3. The seven crystal systems.

System	Possible Variations	Axial distances	Axial angles	Examples
Cubic	Primitive Body-centred Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, KCl, Zinc blende, Cu, Ag
Tetragonal	Primitive Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	White tin, SnO_2, TiO_2, $CaSO_4$
Orthorhombic	Primitive Body-centred Face-centred End-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $PbCO_3$, $BaSO_4$
Monoclinic	Primitive End-centred	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$	Monoclinic sulphur, $PbCrO_4$, $Na_2SO_4 \cdot 10H_2O$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	Graphite, ZnO, BeO, CdS,
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$), $NaNO_3$, cinnabar (HgS), quartz, Sb
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$, H_3BO_3.

It may be noted that all crystals do not have simple lattices *i.e.,* having lattice points only at the corners. In addition, there are some lattices which are different from the simple lattice. For example, if we consider a cubic system, which is simplest of all these seven systems, it is observed that a cube has three types of lattices.

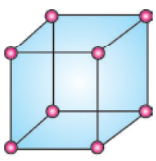
Types of Cubic Lattices

There are three types of cubic unit cells or lattices. These are :

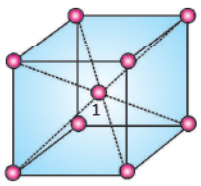
1. Simple or Primitive. *It has points at all the corners of the unit cell.* A primitive cubic unit cell is shown in Fig. 15 (*a*). It consists of one atom at each of the eight corners.

2. Body centred cubic unit cell (*bcc*). *It has points at all the corners as well as at the body centre of the cube* [Fig. 15 (*b*)]. It is labelled as ***bcc***. As shown in the figure, in a body centred cubic unit cell, there are eight atoms at the corners and one at the centre.

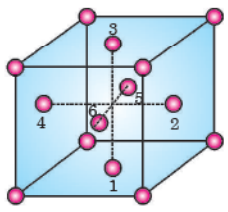
3. Face centred cubic unit cell (*fcc*). In this case, *there are points at all the corners as well as at the centre of each face.* It is shown in Fig 15 (*c*). It is labelled as ***fcc***. As shown in the figure, it has eight atoms at the corners and six atoms at the centre of faces.



(*a*) **Simple or primitive cubic:** Atoms at eight corners only.



(*b*) **Body centred cubic:** Atoms at the corners and at the body centre of the cube. Atom 1 is at the body centre of the cube.



(*c*) **Face centred cubic:** Atoms at the corners and centre of each face. Atoms 1, 2, 3, 4, 5, and 6 are present at the centres of six faces (atom 5 corresponds to atom at the centre of back face and atom 6 corresponds to the centre of front face.)

Fig. 15. Three types of cubic lattices.

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Similarly, if we consider the other lattices, in addition to simple lattices for other systems, it is observed that there are 14 different types of space lattices. These are known as **14 Bravais lattices** after the name of French mathematician who first described them. These are given in Fig. 16.

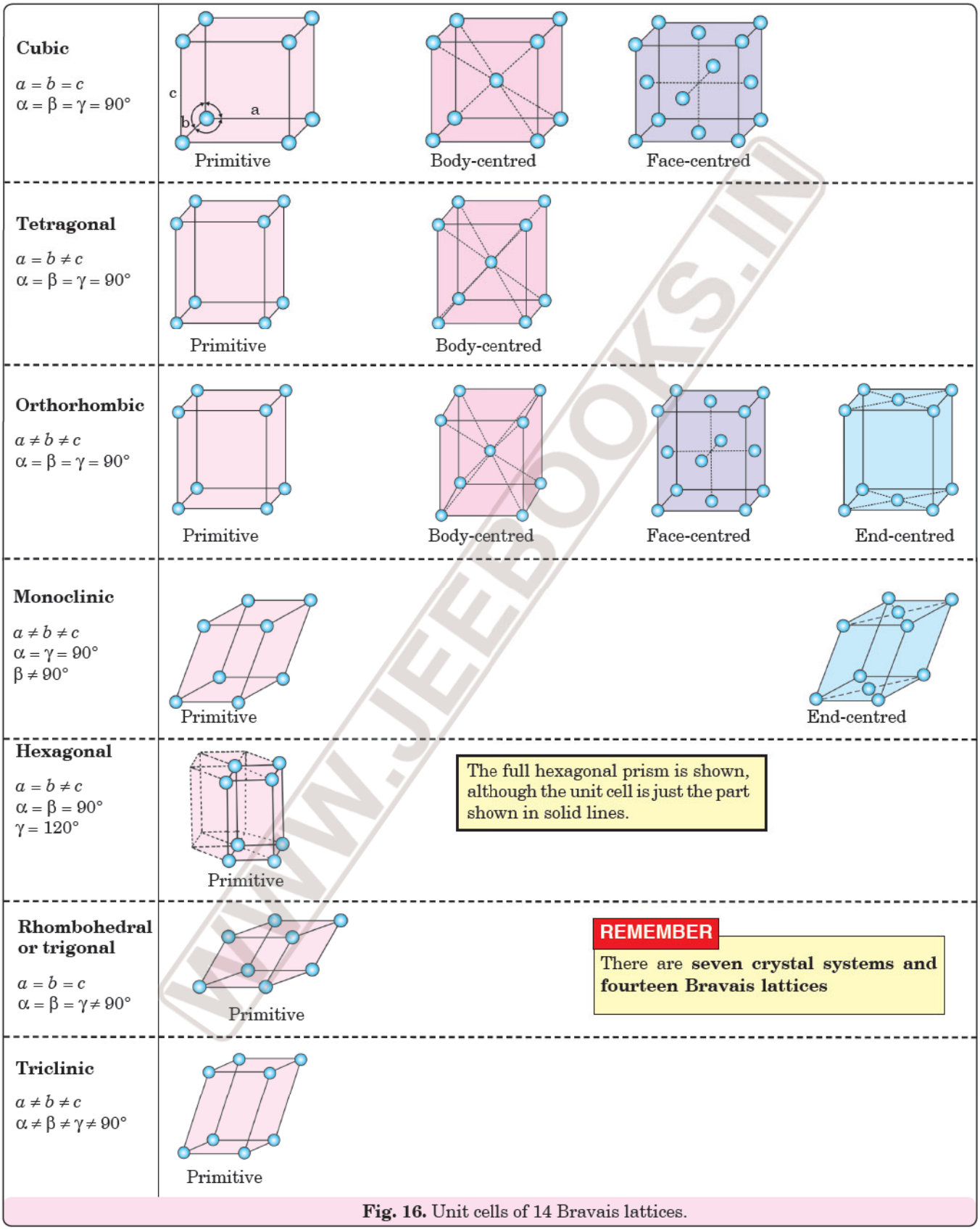

Fig. 16. Unit cells of 14 Bravais lattices.

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NOTE

It may be noted that there is another type of non-primitive unit cell known as **end centred unit cell**. In this case, there are points (or atoms) at all the corners and at the centres of any two opposite faces.

- There is no end centred cubic unit cell.
- Only orthorhombic and monoclinic crystal systems have end centred unit cells.

TYPES OF CUBIC CRYSTALS AND NUMBER OF ATOMS PER UNIT CELL

We know that a crystal lattice is made up of a very large number of unit cells and every lattice point is occupied by one constituent particle (atom, molecule or ion). In different types of unit cells, the particles may be at the corners, at the body centre or, at the centre of faces. Since every unit cell in a crystalline solid is adjacent to other unit cells, most of the atoms (or constituent particles) are shared by neighbouring unit cells. As a result, only some portion of each atom belongs to a particular unit cell. For example, in all types of cubic cells, each corner atom belongs to eight adjacent unit cells as shown in Fig 17(*c*), four unit cells in the same layer and four unit cells of the upper layer. Therefore, only **1/8th of an atom** (or molecule or ion) actually belongs to a particular unit cell.

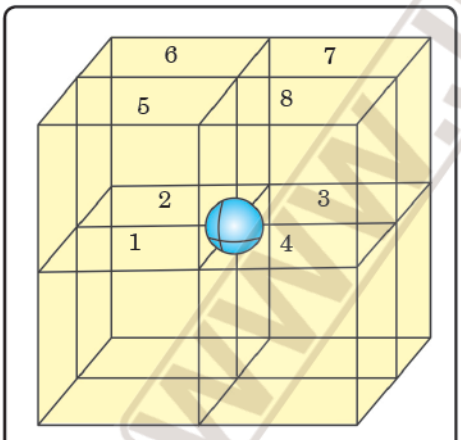

Fig. 17(*a*). A corner atom in cubic unit cell is shared by 8 unit cells.

Similarly, each face centred atom is shared by two unit cells (shown in Fig. 17*b*) and only **1/2 of an atom** (or molecule or ion) belongs to a particular unit cell.

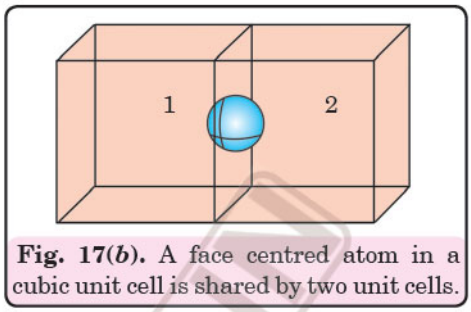

Fig. 17(*b*). A face centred atom in a cubic unit cell is shared by two unit cells.

An atom at the body centre of a unit cell is not shared by other unit cells and it **completely belongs to the unit cell** (Fig. 17*c*).

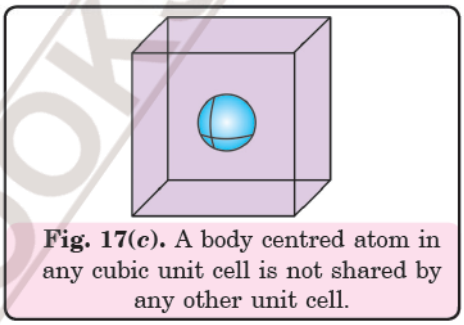

Fig. 17(*c*). A body centred atom in any cubic unit cell is not shared by any other unit cell.

Thus, the contribution of each atom to the unit cell is :

at corner = $\frac{1}{8}$; at the face = $\frac{1}{2}$; within the body = 1

For simplicity assume that the constituent particle is an atom. The unit cell may be represented in **three different ways.**

(*a*) Each small sphere in figure represents only the centre of the particle occupying that position and not its actual size. Such type of structures are called **open structures**. It is easier to follow the arrangement of particles in open structures [Fig. 18 (*a*)].

(*b*) **Space filling representation** of the unit cell with actual particle size [Fig. 18 (*b*)]. This gives a more realistic picture showing how the particles actually pack within the solid.

(*c*) **Actual portion** of different atoms present in a unit cell [Fig. 18 (*c*)].

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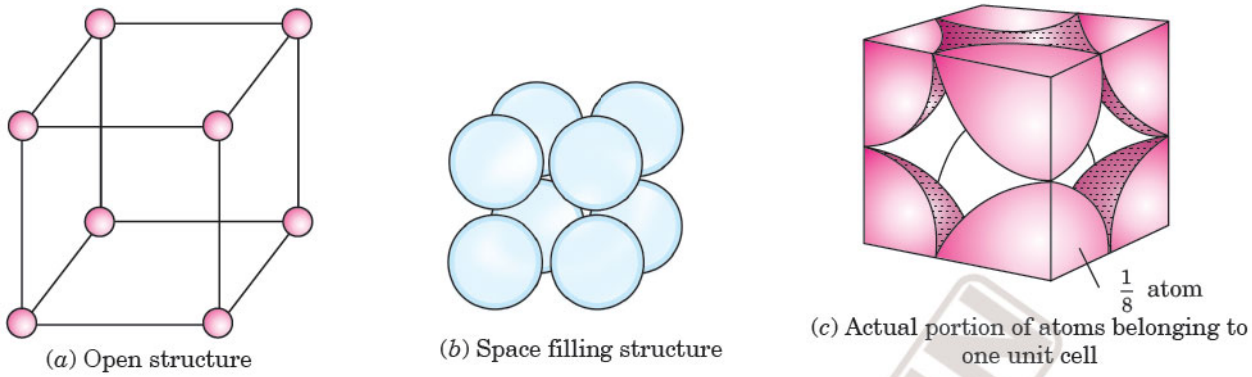


(*a*) Open structure (*b*) Space filling structure (*c*) Actual portion of atoms belonging to one unit cell

Fig. 18. Simple cubic arrangement and number of spheres per unit cell.

Let us now **calculate number of atoms** in different types of cubic unit cells.

(*i*) **Simple** or **primitive cubic unit cell**

In this unit cell, *the points (atoms, ions or molecules) are present at all the corners of a cube.* This is shown in Fig. 18 (*a*). It is clear from Fig. 18 (*c*) that atom present at each corner contributes 1/8 to each cube because it is shared by 8 cubes. Now, there are 8 atoms at the corners.

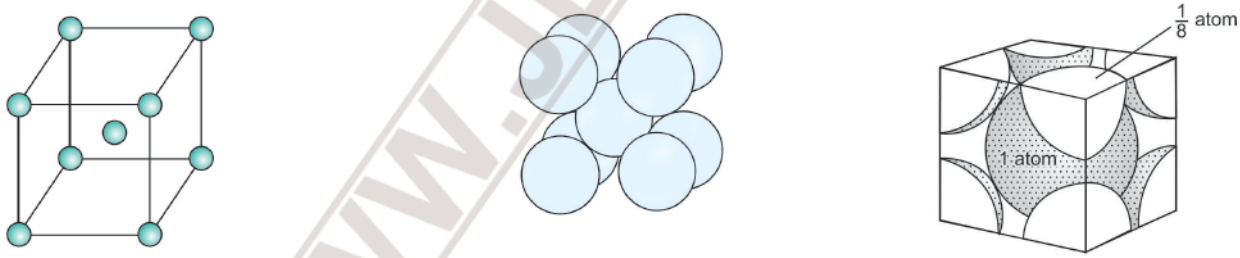
Thus, the number of atoms present in each unit cell

$$= 8 \text{ corner atoms} \times \frac{1}{8} \text{ atom per unit cell} = \mathbf{1 \text{ atom.}}$$

Thus, **simple or primitive cubic unit cell has one atom per unit cell.**

(*ii*) **Body centred cubic unit cell**

It has points at all the corners as well as at the body centre of the cube. It is shown in Fig. 19. It is clear from the figure that there are eight atoms at the corners and each is shared by 8 unit cells so that the contribution of each atom at corner is 1/8. In addition, there is one atom in the body of the cube as shown in Fig. 19 (*c*) which is not shared by any other cube.



(*a*) Open structure (*b*) Space filling structure (*c*) Actual portion of atoms belonging to one unit cell

Fig. 19. Body centred cubic unit cell.

Thus, the number of atoms present at the corners per unit cell

$$= 8 \text{ corner atoms} \times \frac{1}{8} \text{ atom per unit cell} = 1$$

The number of atoms present at the centre of the cube = 1

$\therefore$ Total number of atoms in *bcc* arrangement = 1 + 1 = **2.**

Thus, **a body centred cubic unit cell has two atoms per unit cell.**

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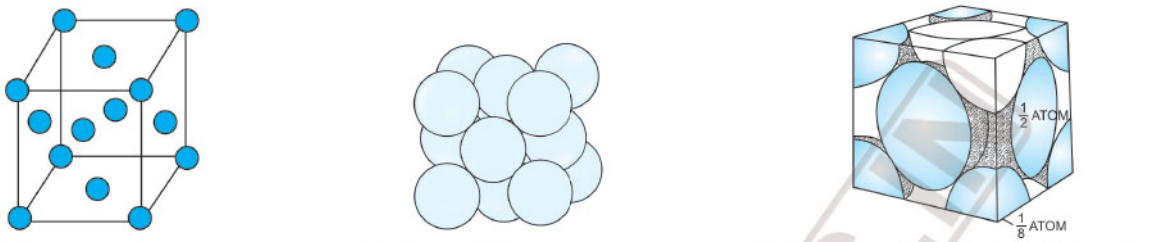
(*iii*) **Face centred cubic unit cell.**

This is also called cubic close packed unit cell. *It has points at all the corners as well as at the centre of each of the six faces.* It is shown in Fig. 20(*a*). In this arrangement, there is one atom at each of the eight corners. It is clear from Fig. 20 (*b*) that atom present at each corner contributes 1/8 to each cube because it is shared by 8 cubes. In addition, there are six atoms at the faces of the cube and each is shared by two unit cells. Therefore, the contribution of each atom at the face per unit cell is 1/2 [Fig. 20 (*c*)].



(*a*) Open structure (*b*) Space filling structure (*c*) Actual portion of atoms belonging to one unit cell

Fig. 20. Cubic close packed or face centred cubic arrangement and share of each atom per unit cell.

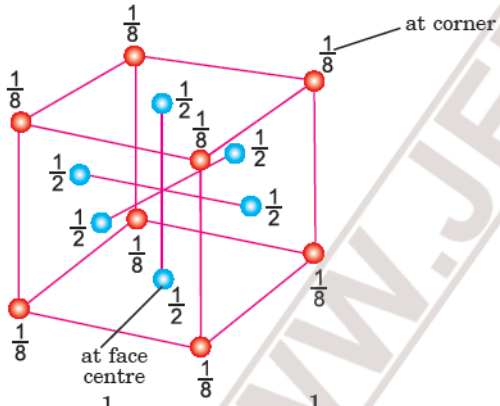
Thus, the number of atoms present at corners per unit cell = 8 corner atoms $\times \frac{1}{8}$ atom per unit cell = 1

The number of atoms present at faces per unit cell = 6 atoms at the faces $\times \frac{1}{2}$ atom per unit cell = 3

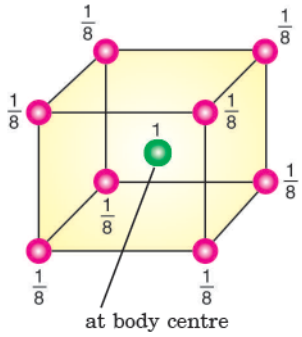
$\therefore$ Total number of atoms in ccp or fcc arrangement = 1+ 3 = 4

Thus, **a face centred cubic unit cell has four atoms per unit cell.**

The contribution of atoms and total number of atoms in different types of cubic unit cells are summarized below :



Contribution $\frac{1}{8}$ at corners and $\frac{1}{2}$ at face centres of the atoms in a face centred cell



Contribution of 1 at the body centre

Fig. 21. Contribution of atoms in a cubic unit cell.

REMEMBER

Unit cell	No. of atoms at corners	No. of atoms at faces	No. of atoms in centre	Total
Simple cubic or primitive cell	$8 \times \frac{1}{8}$	0	0	1
Body centred cubic	$8 \times \frac{1}{8}$	0	1	2
Face centred cubic	$8 \times \frac{1}{8}$	$6 \times \frac{1}{2}$	0	4

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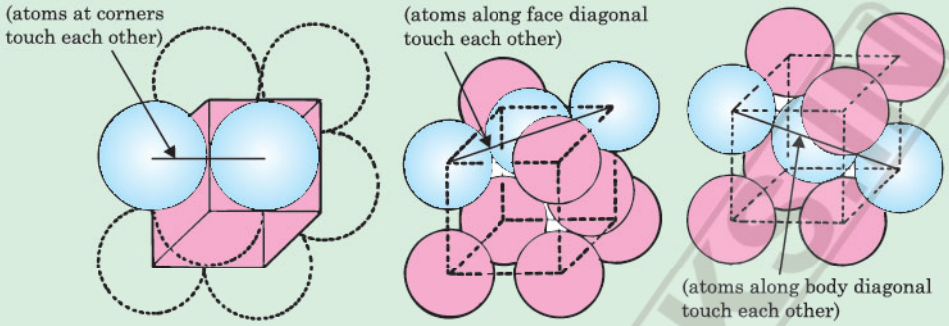
NOTE

It is important to remember that the **atoms (or spheres) at the corners of a simple cube touch each other** [Fig. 22 (*a*)]. However, the atoms at the corners of face centred cube and body centred cube donot touch each other. It may be seen that

- in the face centred cube, the **atoms along the face diagonal of the cube touch each other** [Fig. 22(*b*)].
- in the body centred cube, the **atoms along the body diagonal of the cube touch each other** [Fig. 22(*c*)].

However, for simplicity, the atoms (or spheres) are shown only at the corners in the figures.



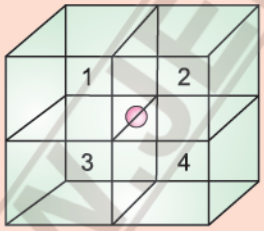
The blue coloured spheres represent the spheres which are touching each other.

(a) Simple cubic (b) Face centred cubic (c) Body centred cubic

Fig. 22

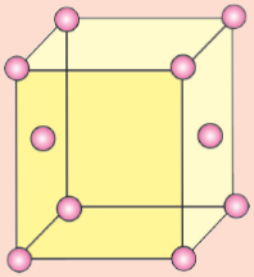
Learning Plus

- **Can you guess the contribution of an atom at the edge centre?**
  An atom present on the edge is shared by four unit cells as shown below:



Therefore, **contribution of each atom on the edge** = 1/4

- **How many atoms will be present in an end centred orthorhombic unit cell?**
  An edge centred orthorhombic unit cell has eight atoms at the corners and two atoms at the centres of two end faces.



Therefore, total number of atoms per unit cell in end centred unit cell is 8 (corners) $\times \frac{1}{8}$ + 2 (end centres) $\times \frac{1}{2}$ = **2 atoms**.

▸ It may be noted that there is **no end centred cubic unit cell.**

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RELATIONSHIP BETWEEN THE NEAREST NEIGHBOUR DISTANCE (d) AND RADIUS OF ATOM (r) AND THE EDGE OF UNIT CELL (a) FOR PURE ELEMENTS

1. Simple cubic

In a simple cubic arrangement, the atoms at the corners touch each other [Fig. 23].

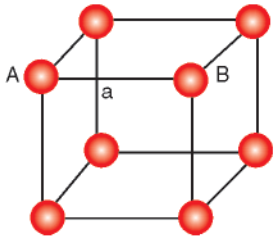

Fig. 23 Simple cubic.

Distance between the nearest neighbours,

$d = AB = a$

Radius, $r = d/2 = a/2$

2. Face centred cubic

In a face centred cubic arrangement, the three atoms along the face diagonal touch each other [Fig. 24].

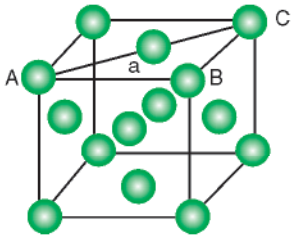

Fig. 24 Face centred cubic.

Distance between the nearest neighbours, $d = \frac{AC}{2}$

Now in right angled ΔABC

$$AC^2 = AB^2 + BC^2$$

$$AC^2 = a^2 + a^2 = 2a^2 \quad \text{or} \quad AC = \sqrt{2}\,a$$

$$\therefore \quad d = \frac{\sqrt{2}\,a}{2} = \frac{a}{\sqrt{2}}$$

Radius, $r = \frac{d}{2} = \frac{a}{2\sqrt{2}}$

3. Body centred cubic

In a body centred cubic arrangement, three atoms along the body diagonal touch each other [Fig. 25].

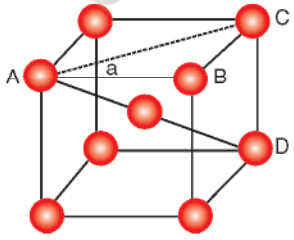

Fig. 25 Body centred cubic.

Distance between nearest neighbours, $d = \frac{AD}{2}$

In right angled ΔABC

$$AC^2 = AB^2 + BC^2$$

$$AC^2 = a^2 + a^2 \text{ or } AC = \sqrt{2}\,a$$

Now in right angled ΔADC,

$$AD^2 = AC^2 + DC^2$$

$$AD^2 = \left(\sqrt{2}\,a\right)^2 + a^2 = 3a^2 \text{ or } AD = \sqrt{3}\,.a$$

$$\therefore \quad d = \frac{\sqrt{3}a}{2}$$

Radius, $r = \frac{d}{2} = \frac{\sqrt{3}}{4}a.$

REMEMBER

The relationship between the nearest neighbour distance and radius of atom (for crystals of pure elements) and the edge of unit cell (a) is summed up below :

Unit cell	Distance between nearest neighbour (d)	Radius (r)
Simple cubic	a	$\frac{a}{2}$
Face centred cubic	$\frac{a}{\sqrt{2}}$ or $0.707\,a$	$\frac{a}{2\sqrt{2}}$ or $0.3535\,a$
Body centred cubic	$\frac{\sqrt{3}}{2}a$ or $0.866\,a$	$\frac{\sqrt{3}}{4}a$ or $0.433\,a$

It may be noted that for pure elements, $r = \frac{d}{2}$.

SOLVED EXAMPLES

❑ Example 3.

A cubic unit cell is made up of X and Y elements. If X are present on the corners of the cube and Y are present on centres of faces of cube, then find the formula of the compound. *(Hr. S.B. 2018)*

Solution : In a cube, X atoms are at the 8 corners, each shared by 8 cubes. Therefore,

The number of X atoms in the unit cell is 8/8 = 1.

Y atoms are at the centres of 6 faces and each face is shared by two cubes. Therefore,

The number of Y atoms = 6/2 = 3

The formula of the compound = XY_3.

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Example 4.

If three elements P, Q and R crystallise in a cubic solid lattice with P atoms at the corners, Q atoms at the cube centres and R atoms at the centre of the edges, then write the formula of the compound.

(Pb. S.B. 2002)

Solution : As P atoms are present at the 8 corners of the cube. Therefore,

No. of P atoms in the unit cell = $8 \times \frac{1}{8} = 1$

Q atoms are present at the cube centres,

No. of Q atoms in the unit cell = 1

R atoms are present at the edges. Since there are 12 edges and atom at each edge is shared by four atoms.

Therefore,

No. of R atoms in the unit cell = $12 \times \frac{1}{4} = 3$

$\therefore$ The formula of the compound = $\mathbf{PQR_3}$.

Example5.

Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a face-centred cubic (f c c) structure. (Atomic mass of Al = 27 g mol^{-1}).

(A.I.S.B. 2017, D.S.B. 2017)

Solution :

$$\text{Moles of aluminium} = \frac{8.1}{27}\text{mol}$$

$$\text{No. of atoms of Al in 8.1 g} = \frac{8.1}{27} \times 6.022 \times 10^{23}$$

No. of atoms in one unit cell = 4(*fcc*)

$$\text{No. of unit cells} = \frac{8.1}{27} \times \frac{6.022 \times 10^{23}}{4}$$

$$= \mathbf{4.5 \times 10^{22}}.$$

Example 6.

Tungsten crystallizes in body centred cubic unit cell. If edge of the unit cell is 316.5 pm, what is the radius of the tungsten atom ?

(D.S.B. 2012, CBSE Sample Paper 2017-18)

Solution : If a is the edge length of *bcc* unit cell, then radius of an atom,

$$r = \frac{\sqrt{3}}{4}a$$

Here, $a = 316.5$ pm

$$\therefore \quad r = \frac{\sqrt{3}}{4} \times 316.5 \text{ pm}$$

$$= \mathbf{137.04\ pm}$$

Example 7.

Aluminium crystallizes in a fcc structure. Atomic radius of the metal is 125 pm. Calculate the edge length of the unit cell of the metal?

(A.I.S.B. 2013, Karnataka S.B.2014)

Solution : In a face centred cubic structure, radius (r), is related to length of the side (a) as:

$$r = \frac{a}{2\sqrt{2}}$$

or $\quad a = 2r\sqrt{2}$

$\quad r = 125$ pm

$\therefore \quad a = 2 \times 125 \times 1.414$

$\quad = \mathbf{353.3\ nm.}$

Practice Problems

1. A cubic solid is made up of two elements X and Y. Atoms Y are present at the corners of the cube and atoms X at the body centre. What is the formula of the compound ?
   (D.S.B.2006, CBSE Sample Paper 2008)
2. When atoms are placed at the corners of all 12 edges of a cube, how many atoms are present per unit cell ?
3. A unit cell consists of a cube in which there are A atoms at the corners and B atoms at the face centres and A atoms are missing from 2 corners in each unit cell. What is the simplest formula of the compound ? *(Pb. S.B. 2011)*
4. A compound of X and Y crystallizes in the cubic structure in which Y atoms are at the corners and X atoms are at the alternate faces of the cube. Find the formula of the compound.
   (Pb. S.B. 2011, Meghalaya S.B. 2013)
5. Gold crystallizes in the face centred cubic lattice. Calculate the approximate number of unit cells in 2 mg of gold. (atomic mass of gold = 197 u).
6. Xenon crystallizes in the face centred cubic lattice and the edge of the unit cell is 620 pm. What is the nearest neighbour distance and radius of xenon atom ?
7. The length of the unit cell edge of a body centred cubic metal crystal is 352 pm. Calculate the radius of an atom of the crystal. *(Nagaland S.B. 2013)*
8. Calculate the atomic radius of elementary silver which crystallises in face centred cubic lattice with unit cell edge length 4.086×10^{-10}m.
   (Assam S.B. 2016)
9. A solid has a structure in which W atoms are present at the corners of the cubic unit cell, O atoms are located at the cube edges and Na atoms are present at cube centres. What is the formula of the compound ?
10. CsCl crystallizes in cubic structure in which Cl^- ions are at the corners and Cs^+ ions occupy centre of the unit cell. If radii of Cs^+ and Cl^- ions are 1.69Å and 1.81Å respectively, calculate the edge length of the unit cell.
11. Tungsten crystallizes in body centred cubic lattice. Calculate the number of unit cells in 1.5 g of tungsten (Atomic mass of tungsten = 184 u).
    (Pb. S.B. 2013)
12. Sodium crystallizes in a *bcc* unit cell. Calculate the approximate number of unit cells in 9.2 g of sodium (Atomic mass of Na = 23 u).
    (C.B.S.E. Sample Paper 2011, Assam S.B. 2013)
13. Gold (atomic radius = 0.144 nm) crystallizes in face centred unit cell. What is the length of the side of the cell? *(Meghalaya S.B. 2017)*

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14. In a face centred cubic arrangement of A and B atoms, A atoms occupy the corners and B atoms occupy the face centres of the unit cell. If one of the atoms is missing from the corner in each unit cell, what is the simplest formula of the compound?

Answers to Practice Problems

1. XY	**2.** 1
3. AB_4	**4.** XY
5. 1.528×10^{18} unit cells	**6.** 438.5 pm, 219.25 pm
7. 152.416 pm	**8.** 1.44×10^{-10} m
9. $NaWO_3$	**10.** 4.04 Å
11. 2.45×10^{21} unit cells	**12.** 1.2044×10^{23} unit cells
13. 0.407 mm	**14.** A_7B_{24}

Hints & Solutions on page 57A

CLOSE PACKED STRUCTURES

In the formation of crystals, the constituent particles (atoms, ions or molecules) get *closely packed together*. The closely packed arrangement is that in which *maximum available space is occupied leaving minimum vacant space*. This corresponds to a state of maximum possible density. The closer the packing, the greater is the stability of the packed system.

We know that the constituent particles of crystals may be of varying shapes and, therefore, the mode of closest packing of particles will vary according to their shapes and sizes. However for understanding, we can use identical hard spheres of equal size to represent atoms in a metal in terms of closest packing of identical spheres.

We can build up the three dimensional structure in three steps :

(*a*) Close Packing in one Dimension

There is only one way of arranging spheres in one dimensional close packed structure in which the spheres are placed in a horizontal row touching each other. This is shown in Fig. 26.

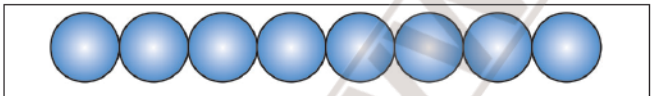


Fig. 26. Close packing of spheres in one dimension.

As can be seen in this arrangement, each sphere is in contact with two of its neighbours.

The *number of nearest neighbours of a particle* is called **its co-ordination number.**

Thus, in one dimensional close packed arrangement, **the coordination number is 2.**

(*b*) Close Packing in two Dimensions

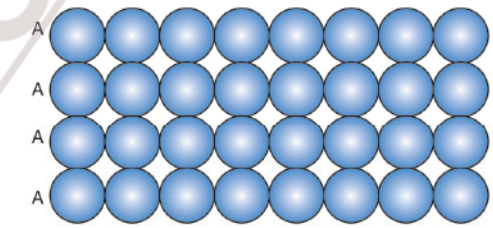
Two dimensional close packed structure can be generated by placing the rows of close packed spheres. The rows can be combined in the following **two ways** with respect to the first row to build a crystal plane.

(*i*) Square close packing or AAA... type arrangement in two dimensions.

The spheres are packed in such a way that the rows have a horizontal as well as vertical alignment. In this arrangement, the spheres of second row are exactly above those of the first row. The second row is exactly same as the first one. If we label the first row as 'A' type, the second row is also 'A' type. Similarly, we may place more rows to get AAA..... type arrangement as shown in Fig. 27 (*a*). In this arrangement, the spheres are found to form squares. This type of packing is also called ***square close packing in two dimensions.***

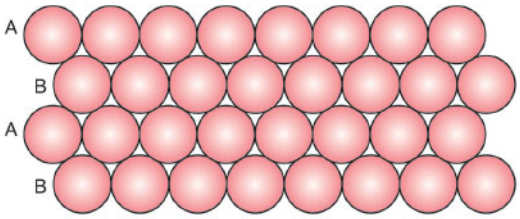
(*ii*) Hexagonal close packing or ABABA... type arrangement in two dimensions.

The spheres are packed in such a way that the spheres in the second row are placed in the depressions between the spheres of the first row. Similarly, the spheres in the third row are placed in the depressions between the spheres of the second row and so on. In this arrangement, the second row is different from the first row. But the spheres in third row are aligned with those of the first row. Similarly, the spheres of fourth row are aligned with those of second row. If the arrangement of spheres in first row is called 'A' type, the one in the second row is different and may be called 'B' type. Now, the arrangement of spheres of third row is same as that of first row, and therefore, it is also called 'A' type. Similarly, fourth row is called 'B' type. Hence the arrangement is called ABAB..... type. This type of arrangement is also called *hexagonal close packing of spheres in two dimensions* and is shown in Fig. 27.(*b*) (arrangement II).



Arrangement I

(*a*) Square close packing occupies 52.4% of available space



Arrangement II

(*b*) Hexagonal close packing occupies 60.4% of available space

Fig. 27. Packing of spheres in two dimensions.

A comparison of two ways of packing of spheres shows that in arrangement I, the spheres are less closely packed than in arrangement II. It has been calculated that in arrangement I, only 52.4% of the available space is occupied by the spheres. In the second arrangement, 60.4% of the space is occupied. Therefore, the arrangement II is more efficient and leaves less space unoccupied by spheres. Thus, arrangement II is more economical and it represents a close packing of spheres.

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It can be seen that in arrangement I, each sphere is in contact with four other spheres as shown in Fig. 28 (*a*). On the other hand, each sphere is in contact with six other similar spheres in arrangement II as shown in Fig. 28 (*b*).

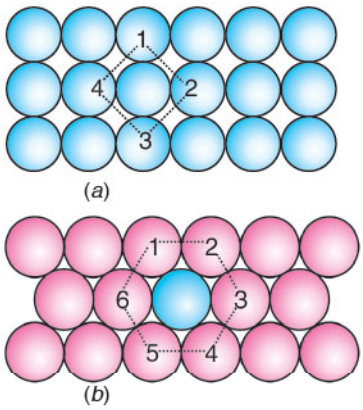

Fig. 28. (*a*) A sphere in square close packing is in contact with four spheres. (*b*) A sphere in hexagonal close packing is in contact with six spheres.

Thus, in two dimensional close packing, the co-ordination number of each sphere in arrangement I (square close packing) is **four** and in arrangement II (hexagonal close packing) is **six**. Thus, the arrangement II represents closest packing of spheres in a layer.

(*c*) Close Packing in Three Dimensions

We can now build other layers over the first layer to extend the packing in three dimensions. This can be done by building layers on square packed and hexagonal close-packed arrangement of first layer. Let us see what types of three dimensional close packing can be obtained from these two types of arrangements. Let us mark the sphere in the first layer as A.

(*i*) Three dimensional close packing from two dimensional square close packed layers

For placing the second square close packed layers above the first row, follow the same procedure that was followed when one row was placed adjacent to the other row. The second layer is placed over the first layer such that these spheres of the second layers are exactly above those of first layer. In this arrangement, spheres of both layers are perfectly aligned horizontally as well as vertically. Similarly, we may place more layers one above the other. This is shown in Fig. 29 (*a*). If the arrangement of spheres in the first layer is called 'A' type, the other layers will also be 'A' type because they have same arrangement. This type of packing is referred to as AAA.....type. This type of packing is also called **simple cubic packing** and its unit cell is the primitive unit cell as shown in Fig. 29 (*b*).

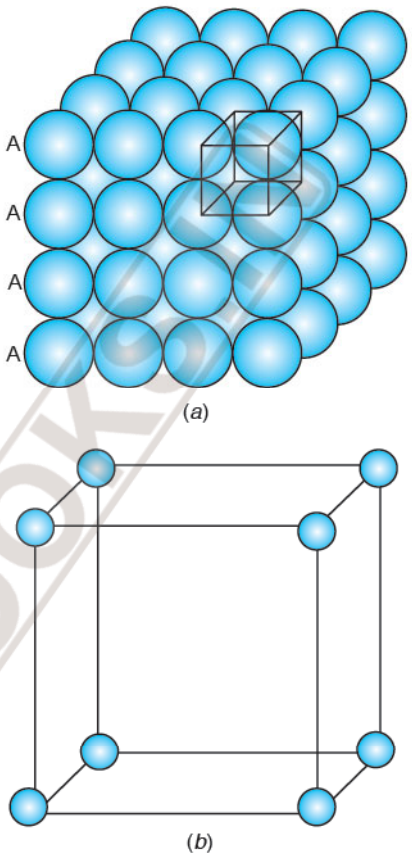

Fig. 29. Simple cubic lattice formed by AAA.... arrangement.

(*ii*) Three dimensional close packing from two dimensional hexagonal close packed layers.

As we have already seen that for two dimensional packing, hexagonal close packing is more efficient packing. Let us consider a three dimensional packing above this layer.

Let us mark the spheres in the first layer as A. It is clear from Fig. 30(*a*) that in the first layer there are some empty spaces or hollows called **voids.** These are triangular in shape. These triangular voids are of two types marked as *a* and *b*. All the hollows are equivalent but the spheres of second layer may be placed either on hollows which are marked *a* or on other set of hollows marked *b*. It may be noted that it is not possible to place spheres on both types of hollows. Let us place the spheres on hollows marked *b* to make the second layer which may be labelled as *B* layer. Obviously the holes marked *a* remain unoccupied

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while building the second layer. The second layer is indicated as dotted circles in Fig. 30 (*b*).

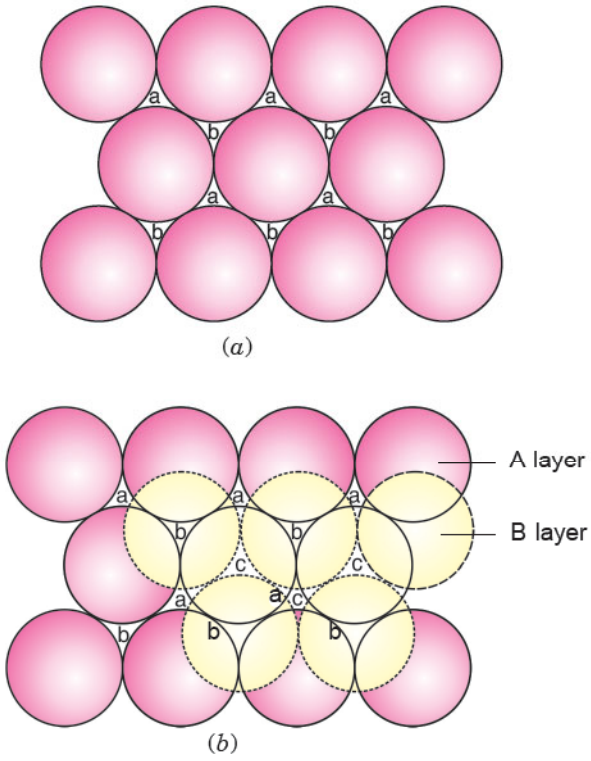

Fig. 30. Packing of second layer (*b*) on first layer (*a*).

It is clear from Fig. 30 (*b*) that the two types of voids are not similar. The '*c*' type of voids are triangular but '*a*' type of voids of the second layer are a combination of two triangular voids (one each of first layer and second layer) with the vertex of one triangle upwards and the vertex of other triangle downwards.

Whenever a sphere of second layer is placed above the void of first layer, a tetrahedral void is formed. These voids are called **tetrahedral voids** because a tetrahedron is formed when the centres of these four spheres are joined. **The voids '*c*' represent tetrahedral voids.**

The voids '*a*' are double triangular voids. The triangular void in the second layer are above the triangular voids in the first layer and the triangular shapes of these voids donot overlap. Such voids are surrounded by six spheres and are called **octahedral voids.**

Now the third layer can be build up by placing spheres above tetrahedral voids marked (*c*) or octahedral voids marked (*a*).

(*i*) Covering tetrahedral voids

When a third layer is to be added, again there are two types of hollows available. One type of hollows marked '*a*' are unoccupied hollows of the first layer. The other type of hollows are hollows in the second layer (marked *c*). Thus, there are **two alternatives** to build the third layer.

The third layer of spheres may be placed on the tetrahedral voids marked (*c*) of the second layer. In this arrangement, the spheres of the third layer lie directly above those in the first layer. In other words, *third layer becomes exactly identical to the first layer* (labelled A). This is shown in Fig. 31. This type of packing is referred to as ABABA.... arrangement. This type of packing is also known as **hexagonal close packing.** It is abbreviated as ***hcp***. For simplicity, *hcp* arrangement can be drawn as shown in Fig. 31 (*b*).

Metals like magnesium, molybdenum, beryllium, zinc, etc. adopt this type of arrangement.

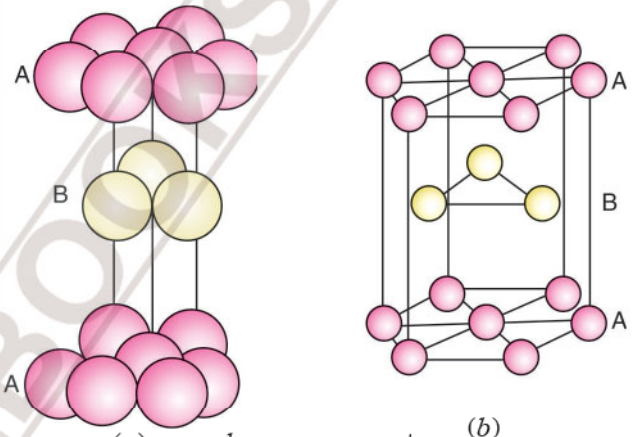

Fig. 31. ABABA... or *hcp* arrangement of spheres. Metals like magnesium, zinc, etc. adopt this type of arrangement.

(*ii*) Covering octahedral voids

The second way to pack spheres in the third layer is to place them over octahedral voids marked '*a*' (unoccupied hollows of first layer). This gives rise to a new layer labelled as C. However, it can be shown that the spheres in the fourth layer will correspond to those in the first layer. This is shown in Figs. 32 (*a*) and 32 (*b*). This gives the ABCABCA.....type of arrangement. It is also known as **cubic close packing** and is abbreviated as ***ccp.*** For simplicity ccp arrangement can be drawn as shown in Fig. 32(*c*). It is clear from Fig. 32 (*c*) that there is *a* sphere at the centre of each face of the cube. Therefore, this arrangement is also known as **face centred cubic arrangement** and is abbreviated as ***fcc.*** Metals like copper, iron, nickel, aluminium, gold and silver crystallise in this type of structure.

It may be noted that both types of packing are equally economical though these have different forms. In both cases, 74% of the available volume is occupied by the spheres.

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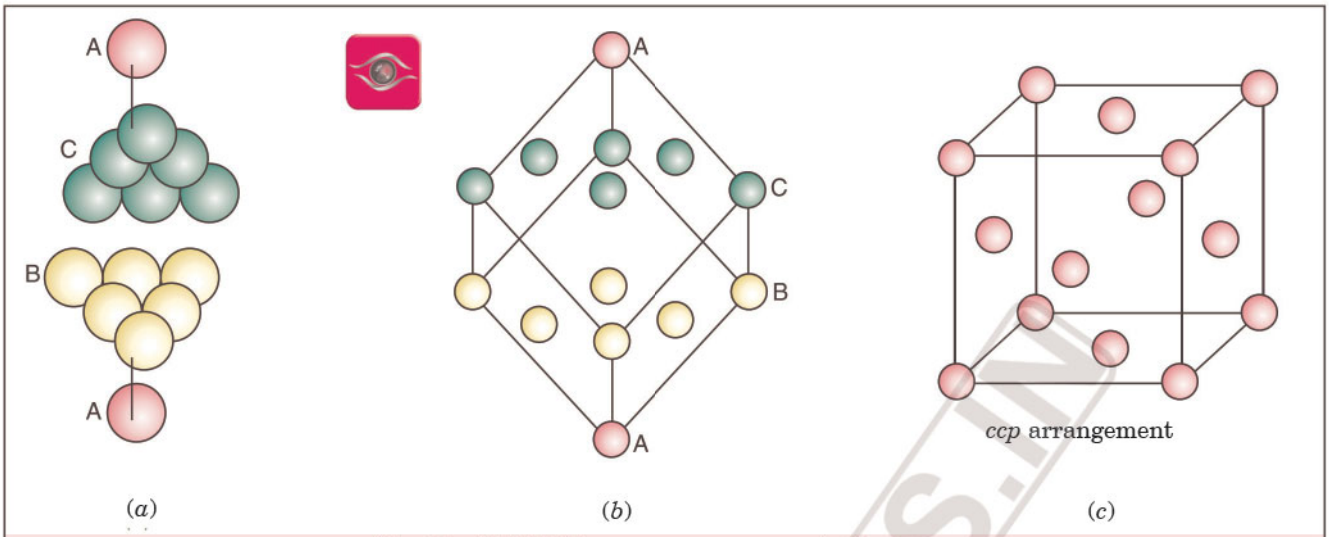

Fig. 32. ABCABCA... or *ccp* arrangement of spheres.

Learning Plus

- **Number of atoms per unit cell in *hcp*.**

❑ In *hcp* arrangement, Fig. 31 (*b*), there are 12 atoms at the corners, 2 at face centres and 3 atoms are present in the body. In *hcp*, each corner is shared by six unit cells, therefore, contribution of atom at the corner is 1/6; each atom at the face centre is shared by 2 unit cells and therefore, contribution of atom at the face centre is 1/2; the atom within the body contributes to that unit cell only. Thus,

No. of atoms per unit cell =

$$12 \text{ (at corners)} \times \frac{1}{6} + 2 \text{ (face)} \times \frac{1}{2} + 3 \text{ (body)} \times 1$$

$$= 2 + 1 + 3 = 6 \text{ atoms/unit cell.}$$

INTERSTITIAL VOIDS OR INTERSTITIAL SITES

In the close packing of spheres, certain hollows or voids are left vacant. These holes or voids in the crystals are called **interstitial voids** or **interstitial sites.** Two important interstitial voids are (*i*) *tetrahedral* (*ii*) *octahedral.*

We have learnt during packing of spheres that after arranging two layers (A and B) we find two types of voids (marked *a* and *c*). The void '*c*' is created by four spheres and is called tetrahedral void. The void '*a*' is created by six spheres in contact and is called octahedral void. These are shown in Fig. 33 marking them as *t* and *o*.

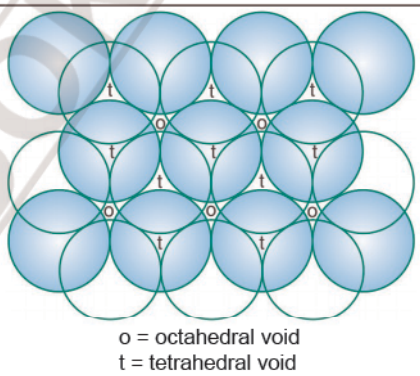

Fig. 33. Tetrahedral and octahedral voids in close packing arrangement.

(*i*) **Tetrahedral void or site .** A sphere in the second layer is placed above three spheres touching one another in the first layer. This is shown in Fig.34. The centres of these spheres lie at the apices of a tetrahedron. It may be noted that the shape of the void is not tetrahedral, but the arrangement around this void is tetrahedral. Thus, *the vacant space among four spheres having tetrahedral arrangement* is called **tetrahedral void** or **tetrahedral site.**

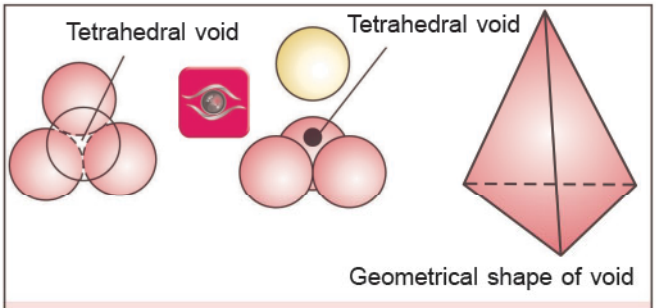

Fig. 34. Tetrahedral void.

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(*ii*) **Octahedral void or site.** This type of void or site is formed at the centre of six spheres. It is shown in Fig. 35.

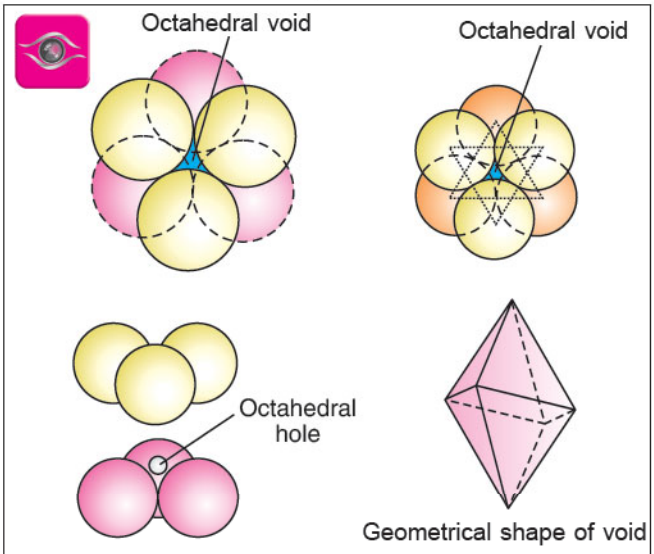


Fig. 35. Octahedral void.

From the figure, it is clear that each octahedral void is produced by two sets of equilateral triangles which point in opposite directions. Thus, *the void formed by two equilateral triangles with apices in opposite direction* is called **octahedral void** or **octahedral site**. This void is, therefore, surrounded by 6 spheres lying at the vertices of a regular octahedron.

Number of octahedral and tetrahedral voids or sites. There are two tetrahedral voids for each sphere and there is only one octahedral void for each sphere. Thus, in a close packed structure of N spheres, there are :

tetrahedral voids = 2N
octahedral voids = N
total number of tetrahedral and octahedral voids = 3N

Learning Plus

The presence of interstitial voids or interstitial sites play an important role in chemistry of transition metals. The transition metals can easily accommodate the small non-metallic atoms such as hydrogen, boron, carbon and nitrogen because of spaces between the metal atoms. These compounds are called **interstitial compounds.**

Coordination Number

The number of spheres which are touching a given sphere is called **the coordination number.** Thus, **coordination number** is

the number of closest (or nearest) neighbours of any constituent particle in the crystal lattice.

As already discussed in *hcp* and *ccp* arrangements, a sphere is in direct contact with 6 other spheres in the same plane of the central atom. It touches three spheres in the layer above it and three spheres in the layer below it. Thus, its coordination number in *hcp* and *ccp* arrangements is 12 as shown in Fig. 36.

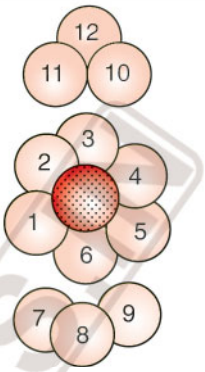


Fig. 36. Coordination number of 12 in *hcp* and *ccp* arrangement.

It may be noted that coordination numbers of 4, 6, 8 and 12 are very common in various types of crystals.

EFFICIENCY OF PACKING OR PACKING EFFICIENCY

In whatever way, the constituent particles (atoms, molecules or ions) are packed, there is always some free space left in the form of voids. The **packing efficiency** is

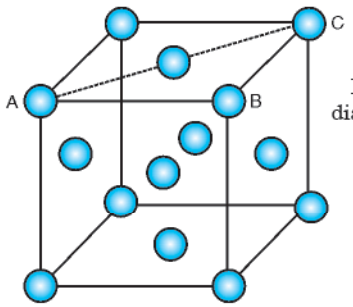
the percentage of total space filled by the particles.

Alternatively, it may also be expressed as **packing fraction. It is the fraction of total space filled by the particles.** Both types of close packing (*hcp* and *ccp*) are equally efficient and occupy 74% of the available volume. On the other hand, in body centred cubic structure, the efficiency is 68% while in simple cubic structure, it is only 52.4%.

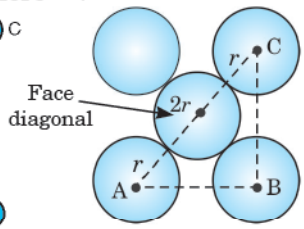
Let us calculate the packing efficiencies in different structures.

(*a*) In cubic close packing or face centred cubic arrangement

Suppose the edge length of the unit cell = a
and radius of each sphere = r



ccp arrangement



top view of *ccp* arrangement (spheres along face diagonal are touching)

It is clear from the figure that there are 8 spheres at the corners and six spheres at the faces.

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No. of spheres in unit cell $= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

As spheres along face diagonal are touching, it is evident from the figure,

$$AC = 4r$$

Consider ΔABC. Since it is right angled triangle,

$$AC^2 = AB^2 + BC^2 = a^2 + a^2 = 2a^2$$

$\therefore$ Face diagonal, $AC = \sqrt{2} \, . \, a$

$$\therefore \sqrt{2} \, .a = 4r \text{ or } a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}\, r$$

Volume of a unit cell

$$= a^3 = (2\sqrt{2}\, r)^3 = 16\sqrt{2}\, r^3$$

Total volume of 4 spheres

$$= 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$$

Packing efficiency

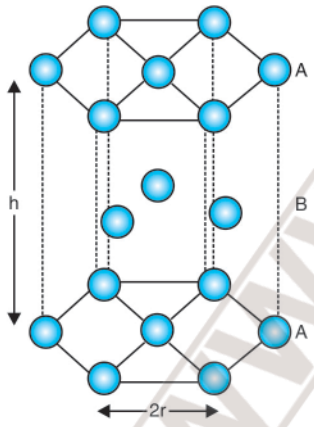
$$= \frac{\text{Volume of four spheres in the unit cell}}{\text{Total volume of unit cell}} \times 100$$

$$= \frac{\frac{16}{3}\pi r^3}{16\sqrt{2}\, r^3} \times 100$$

$$= \frac{\pi}{3\times\sqrt{2}} \times 100 = \frac{3.142}{3\times 1.414} \times 100 = 74\%$$

$\therefore$ **Volume occupied in *fcc* or *ccp* arrangement = 74%**

(*b*) In hexagonal close packing (*hcp*) arrangement



hexagonal close packed arrangement

Suppose radius of each sphere $= r$

From the figure, it is clear, that $a = 2r$

Volume of unit cell can be calculated as:

Volume of unit cell = Base area × Height (h)

Base area of regular hexagon = 6 × Area of equilateral triangle

$$= 6 \times \frac{\sqrt{3}}{4} a^2$$

$$= 6 \times \frac{\sqrt{3}}{4} (2r)^2 = 6 \times \sqrt{3}\, r^2$$

Height of unit cell $= 4r.\sqrt{\frac{2}{3}}$

Volume of unit cell $= 6\sqrt{3}\, r^2 \times 4r.\sqrt{\frac{2}{3}} = 24\sqrt{2}\, r^3$

No. of atoms in *hcp* unit cell $= 12 \times \frac{1}{6}$(corners) + 2 $\times \frac{1}{2}$(face centres) + 3 (in body) = 6

Volume of 6 spheres $= 6 \times \frac{4}{3}\pi r^3 = 8\pi r^3$

Packing efficiency

$$= \frac{\text{Volume occupied by spheres in unit cell}}{\text{Volume of } hcp \text{ unit cell}} \times 100$$

$$= \frac{8\pi r^3}{24\sqrt{2}\, r^3} \times 100 = \frac{\pi}{3\sqrt{2}} \times 100 = \frac{3.142}{3\times 1.414} \times 100$$

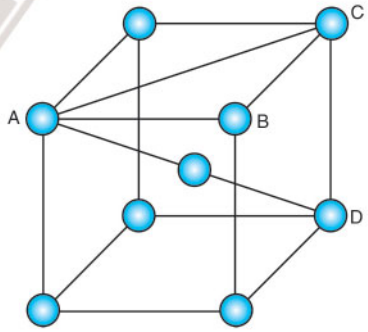
$$= 0.74 \times 100 = 74\%$$

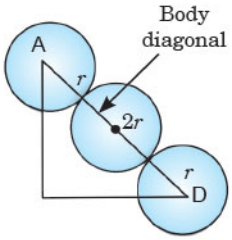
$\therefore$ **Volume occupied in hcp arrangement = 74%**

(*c*) In body centred cubic (*bcc*) arrangement

Suppose the edge length $= a$

Radius of each sphere $= r$





View of body diagonal AD

bcc arrangement (spheres along body diagonal are touching)

It is clear from figure that there are 8 spheres at the corners and one in the body of the unit cell.

No. of spheres per unit cell

$$= 8 \times \frac{1}{8} + 1 = 2$$

It is evident from the figure that spheres along body diagonal are touching so that,

$$AD = 4r$$

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Consider right angled ΔABC,

$$AC^2 = AB^2 + BC^2 = a^2 + a^2$$

$$\therefore \quad AC^2 = 2a^2$$

Similarly in right angled ΔACD,

Body diagonal, $AD^2 = AC^2 + CD^2$

$$AD^2 = 2a^2 + a^2 = 3a^2$$

$$\therefore \quad AD = \sqrt{3}.a$$

$$\therefore \quad \sqrt{3}.a = 4r$$

$$\text{or} \quad a = \frac{4r}{\sqrt{3}}$$

Volume of unit cell $= a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 = \frac{64r^3}{3\sqrt{3}}$

Volume of a sphere $= \frac{4}{3}\pi r^3$

Total volume of two spheres $= 2 \times \frac{4}{3}\pi r^3 = \frac{8}{3}\pi r^3$

Packing efficiency

$$= \frac{\text{Volume of two spheres in the unit cell}}{\text{Total volume of unit cell}} \times 100$$

$$= \frac{\frac{8}{3}\pi r^3}{\frac{64}{3\sqrt{3}} r^3} \times 100 = \frac{\pi\sqrt{3}}{8} \times 100$$

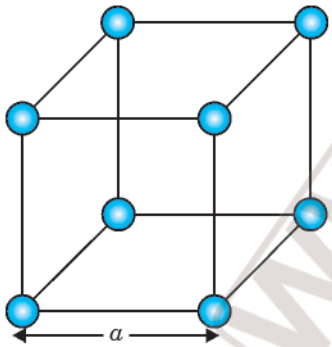
$$= \frac{3.142 \times 1.732}{8} \times 100 = 68\%$$

$\therefore$ **Volume occupied in *bcc* arrangement = 68%**

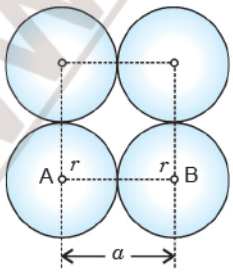
(*d*) In a simple cubic unit cell

Suppose the edge length of the unit cell = a

Radius of the sphere = r



simple cubic arrangement



(spheres along the edge are touching)

Since the spheres are touching each other along the edge, $a = 2r$

Now, there are eight spheres at the corners of the cube.

Each sphere at the corner is shared by eight unit cells and the contribution per unit cell is 1/8 so that

Number of spheres per unit cell is $8 \times \frac{1}{8} = 1$

Volume of sphere $= \frac{4}{3}\pi r^3$

Volume of cube $= a^3 = (2r)^3 = 8r^3$

Packing efficiency

$$= \frac{\text{Volume of one sphere}}{\text{Total volume of cubic unit cell}} \times 100$$

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100$$

$$= \frac{\pi}{6} \times 100 = \frac{3.142 \times 100}{6}$$

$$= 52.37\% \quad \text{or} \quad 52.4\%$$

$\therefore$ **Volume occupied in simple cubic arrangement = 52.4%**

SIZES OF TETRAHEDRAL AND OCTAHEDRAL VOIDS

As we have already learnt, in the close packed structures (*hcp* or *ccp*), there are two common types of voids :

(*i*) octahedral voids

(*ii*) tetrahedral voids

The radii of the voids in these close packed structures are related to the sizes of the spheres present in the packing. Let us calculate the radii of these voids in relation to the radii of the atoms in close packing.

Relationship between radius of octahedral void and radius of atoms in close packing.

An octahedral void is shown in Fig. 37. Though an octahedral void is surrounded by six spheres, only four are shown. The spheres present above and below the void are not shown. Let us assume that the length of the unit cell is a cm and radius of octahedral void (shown by sphere) is r and the radius of sphere is R.

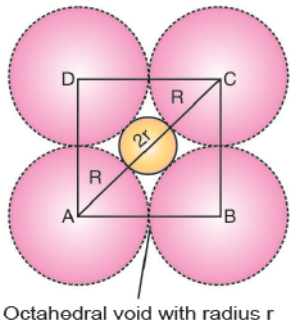


Fig. 37. A cross-section of an octahedral void.

If the length of the unit cell is a cm, then

In right angled ΔABC,

AB = BC = a cm

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The diagonal AC is :

$$AC = \sqrt{AB^2 + BC^2}$$

$$= \sqrt{a^2 + a^2} = \sqrt{2}\, a$$

also $$\frac{AC}{AB} = \frac{\sqrt{2}\, a}{a}$$

$$= \frac{\sqrt{2}}{1}$$

Now, $$AB = 2R$$

$$AC = R + 2r + R = 2R + 2r$$

$$\therefore \quad \frac{2R + 2r}{2R} = \frac{\sqrt{2}}{1}$$

or $$1 + \frac{r}{R} = \frac{\sqrt{2}}{1}$$

or $$\frac{r}{R} = \sqrt{2} - 1 = 1.414 - 1 = 0.414$$

or $$r = 0.414\, R$$

Thus, *for an atom to occupy an octahedral void, its radius must be 0.414 times the radius of the sphere.*

Relationship between radius of the tetrahedral void and radius of atoms in close packing.

A tetrahedral void may be represented by placing four spheres at the alternate corners of a cube as shown in Fig. 38.

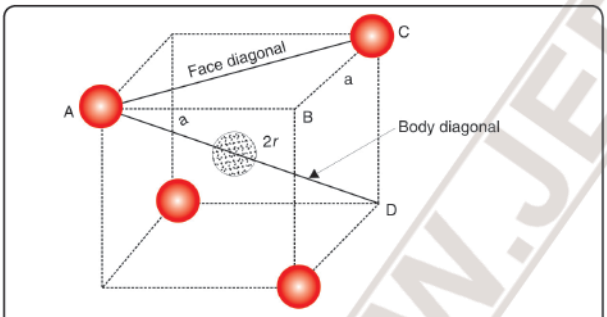

Fig. 38. A tetrahedral void.

It may be noted that a stable tetrahedral arrangement has four spheres at the corners touching each other. However, for simplicity, the spheres are shown by distant circles. Actually all the spheres are touching one another. Let us assume that the length of each side of the cube is a cm and radius of tetrahedral void (shown by a sphere) is r and the radius of sphere is R.

In the figure, AC is a face diagonal.

In right angled ΔABC,

$$AC^2 = AB^2 + BC^2$$

or $$AC = \sqrt{AB^2 + BC^2}$$

$$= \sqrt{a^2 + a^2} = \sqrt{2}\, a$$

As spheres A and C at the face diagonal (though shown by distant circles) are actually touching each other so that

$$AC = R + R = 2R$$

$$\therefore \quad 2R = \sqrt{2}\, a \text{ or } R = \frac{\sqrt{2}a}{2} \qquad ...(i)$$

Now in the right angled triangle, ΔACD, AD is body diagonal and

$$AD^2 = AC^2 + CD^2$$

$$AD = \sqrt{AC^2 + CD^2} = \sqrt{2a^2 + a^2} = \sqrt{3}\, .a$$

The tetrahedral void is present at the centre of the body diagonal AD so that half the length of this diagonal is equal to the sum of the radii of R and r. Thus,

$$R + r = \frac{AD}{2} = \frac{\sqrt{3}a}{2} \qquad ...(ii)$$

Dividing eq. (ii) by eq. (i), we get

$$\frac{R + r}{R} = \frac{\sqrt{3}a}{2} \times \frac{2}{\sqrt{2}a} = \frac{\sqrt{3}}{\sqrt{2}}$$

$$1 + \frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}}$$

or $$\frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}} - 1 = \frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}}$$

$$= \frac{1.732 - 1.414}{1.414} = 0.225$$

or $$r = 0.225\, R$$

Thus, *for an atom to occupy a tetrahedral void, its radius must be 0.225 times the radius of the sphere.*

Thus, **we observe that a tetrahedral void is much smaller than the octahedral void.**

Radius Ratio of Cations and Anions and Stability of Ionic Solids

In case of ionic solids, usually anions are present in the close packed arrangement and cations occupy voids. ***The number of oppositely charged ions surrounding each ion*** is called its **coordination number**. Therefore, the relation between the size of the void and the sphere in the close packed arrangement is expressed in terms of radius of cation to that of anion.

The ratio of the radius of the cation to the radius of the anion is called **radius ratio.**

Thus, $$\text{Radius ratio} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}} = \frac{r_+}{r_-}$$

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For cations occupying the tetrahedral voids,

$r_+ = 0.225\ r_-$ or $r_+/r_- = 0.225$

For cations occupying the octahedral voids,

$r_+ = 0.414\ r_-$ or $r_+/r_- = 0.414$

The ratio of the radius of cation and the radius of anion *i.e.*, radius ratio (r_+/r_-) plays an important role in determining the structures of ionic solids and coordination number of ions. As is clear, for the cations to occupy tetrahedral void, the limiting lowest value of r_+/r_- is 0.225 and to occupy octahedral void, it is 0.414. In other words, for tetrahedral coordination, the radius ratio should be in the range of 0.225 – 0.414. Similarly, it has been calculated that for stable arrangement of cations occupying octahedral voids (*i.e.*, coordination number 6), the radius ratio should be more than 0.414 in the range of 0.414–0.732. If the radius ratio (r_+/r_-) is more than 0.732 (in the range 0.732–1.0), the cations occupy cubic voids (coordination number 8). Similarly, below 0.225, the cations occupy simple trigonal voids. The possible coordination numbers and structural arrangements of anions around cations for different r_+/r_- values are given below :

Radius ratio (r_+/r_-)	Possible coordination number arrangement	Structural	Structural type	Examples
0.155 – 0.225	3	Trigonal planar	B_2O_3	B_2O_3
0.225 – 0.414	4	Tetrahedral	ZnS	ZnS, CuCl, CuBr, CuI BaS, HgS
0.414 – 0.732	6	Octahedral	NaCl	NaCl, MgO, NaBr, CaS, CaO
0.732 – 1.0	8	Cubic	CsCl	CsCl, CsBr, TlBr, NH_4Br

The application of radius ratio rule may be illustrated by the following examples :

SOLVED EXAMPLES

❑ **Example 8.**

The radius of Na^+ ion is 95 pm and that of Cl^- ion is 181 pm. Predict whether the coordination number of Na^+ ion is 6 or 4. ***(Pb. S.B. 2017)***

Solution : Radius of Na^+ = 95 pm

Radius of Cl^- = 181 pm

$$\text{Radius ratio, } \frac{r_+}{r_-} = \frac{r(Na^+)}{r(Cl^-)} = \frac{95}{181} = 0.524$$

The radius ratio lies between 0.414 – 0.732. Hence, Na^+ ions prefer to occupy **octahedral holes** having coordination number 6.

❑ **Example 9.**

Br^- ions form a close packed structure. If the radius of Br^- ion is 195 pm, calculate the radius of the cation that just fits into the tetrahedral hole. Can a cation having a radius of 82 pm be slipped into the octahedral hole of the crystal A^+Br^- ? ***(A.I.S.B. 2003)***

Solution : Radius of the cation just fitting into the tetrahedral hole

= Radius of tetrahedral hole = $0.225 \times r_{Br^-}$

= 0.225×195 = **43.875 pm**

For the cation A^+ with radius, 82 pm

$$\text{Radius ratio} = \frac{r_+}{r_-} = \frac{82\text{ pm}}{195\text{ pm}} = 0.4205$$

Since the radius ratio (r_+/r_-) lies in the range 0.414–0.732, hence the cation A^+ can be slipped into octahedral hole of the crystal A^+Br^-.

Practice Problems

15. The atomic radii of Cs^+ and Cl^- ions are 1.69 Å and 1.81 Å respectively. Predict the coordination number of Cs^+ ion and structure of CsCl.

16. A solid AB has NaCl structure. If the radius of cation A is 100 pm, what is the radius of anion B ? *(Pb.S.B.2017)*

17. If the radius of Br^- ion is 0.182 nm, how large a cation can fit in each of the tetrahedral hole ?

Answers to Practice Problems

15. 8, cubic

16. 136.6 to 241.6 pm.

17. $< 7.53 \times 10^{-2}$ nm

Hints & Solutions on page 57A

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FORMULA OF A COMPOUND AND NUMBER OF VOIDS FILLED

In the case of simple ionic compounds, generally two types of arrangements are possible. These are *cubic close packed* (*ccp*) or *face centred cubic* (*fcc*) arrangement and *hexagonal close packed* (*hcp*) *arrangement*. The larger ions (*i.e.,* anions) adopt these arrangements. The other kinds of ions (*i.e.,* cations) occupy different voids. As we have learnt, there are two types of voids : tetrahedral and octahedral; which are generally occupied.

From the description of the close packed structures and the types of voids occupied, we can easily draw inferences regarding the structures of simple ionic compounds. For example, consider a compound of general formula AB in which the B ions form a close packed lattice. There are two possibilities:

(*i*) Since there is only one octahedral void per atom in a close packed lattice, all the octahedral voids will be occupied by A^+ ions. In this case, the number of A^+ ions and B^- ions will be same. Sodium chloride has this type of structure in which Cl^- ions form a cubic close packed structure and Na^+ ions occupy all the octahedral voids.

(*ii*) There are two tetrahedral voids per atom in a close packed lattice. This means that there are two tetrahedral voids available for every B^- ion. To form the compound AB, only one half of the tetrahedral voids will be occupied. Zinc blende (ZnS) has this type of structure, in which S^{2-} ions form cubic close packed lattice and Zn^{2+} ions occupy one half of the tetrahedral voids.

If, on the other hand, the formula of the compound is A_2B in which B^- ions adopt cubic close packed lattice, then all the tetrahedral voids will be occupied by A^+ ions. Since there are two tetrahedral voids per atom, and all the voids are occupied, there will be two A^+ ions for each B^- ion. Sodium oxide adopts this type of structure. This structure is also known as **antifluorite structure**.

Alternatively, if A^+ ions (though smaller in size than B^- ions) adopt cubic close packed structure and B^- ions occupy all the tetrahedral voids, then the formula of the compound is AB_2. Calcium fluoride has similar type of structure. The structure is known as **fluorite structure**.

The structures of some common ionic solids are summed up in Table 4.

Competition Plus

The arrangement of atoms, ions or molecules in crystals is determined by X-rays diffraction studies. For detail, refer **Competition File** (Page 78A).

Table 4. Summary of the structures of ionic solids.

Compound	Description	Co-ordination number	Other Examples
NaCl	*ccp* arrangement of Cl^-, Na^+ in all the octahedral sites	$Na^+ = 6$ $Cl^- = 6$	Li, Na, K halides, AgCl, AgBr, MgO, CaO
ZnS (Zinc blende)	*ccp* arrangement of S^{2-}, Zn^{2+} in alternative tetrahedral sites	$Zn^{2+} = 4$ $S^{2-} = 4$	BeS, CuCl, CuBr, CuI
CsCl	Simple cubic arrangement of Cl^-, Cs^+ in cubic sites	$Cs^+ = 8$ $Cl^- = 8$	CsBr, CsI TlCl, TlBr
CaF_2	*ccp* arrangement of Ca^{2+}, F^- occupy all tetrahedral sites	$Ca^{2+} = 8$ $F^- = 4$	SrF_2, BaF_2, CaF_2, CdF_2
Na_2O	*ccp* arrangement of O^{2-}, Na^+ occupy all tetrahedral sites	$Na^+ = 4$ $O^{2-} = 8$	Li_2O, K_2S

Effect of Temperature and Pressure on Crystal Structures

At ordinary temperatures and pressures, chlorides, bromides and iodides of Li, Na, K and Rb as well as some of the halides of silver possess the sodium chloride type structure. In this, the coordination number of both the negative and positive ions are 6 : 6. On the application of high pressure, these change to CsCl type structure in which the coordination number of ions become 8 : 8. Therefore, **the high pressure increases the coordination number.** On the other hand, on heating to about 760 K, the CsCl structure transforms to the NaCl structure.

$$\underset{(6:6\text{ coordination})}{\text{NaCl structure}} \underset{760K}{\overset{\text{High pressure}}{\rightleftharpoons}} \underset{(8:8\text{ coordination})}{\text{CsCl structure}}$$

Similarly, NH_4Cl, NH_4Br and NH_4I transform from CsCl structure to the NaCl structure at 457 K, 411 K and 253 K respectively.

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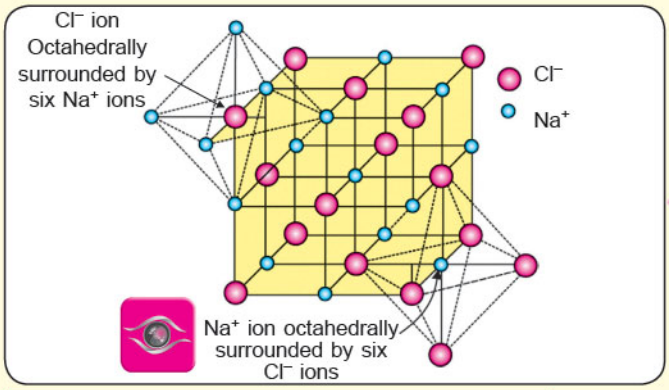
STRUCTURES OF SOME COMMON IONIC COMPOUNDS



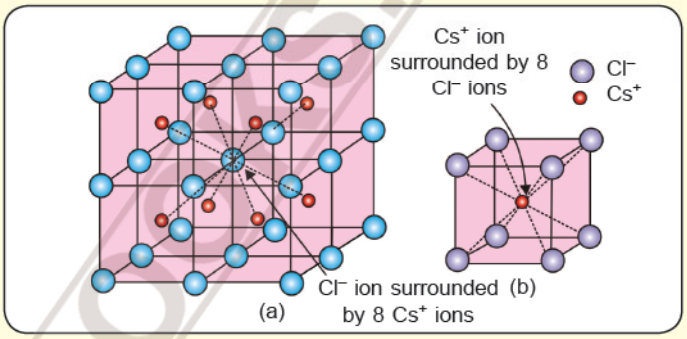
Sodium chloride (NaCl)

Sodium chloride (NaCl)

- **Cl^- ions have ccp or fcc arrangement (*i.e.* Cl^- ions occupy all the corners and all the face centres of the cube)**
- **Na^+ ions occupy all octahedral sites (*i.e.* Na^+ ions are present at the body centre and edge centres)**
- **C.N. of Na^+ = 6**
- **C.N. of Cl^- = 6**

Cesium chloride (CsCl)

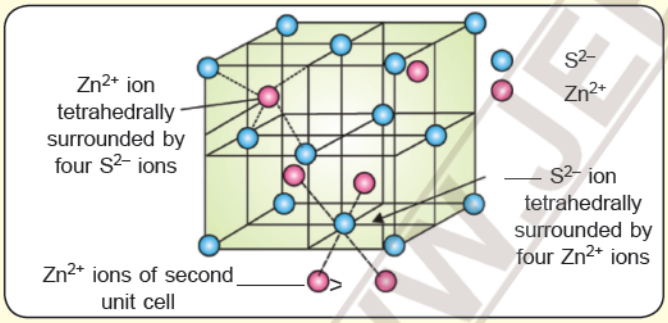
- **Cl^- ions have simple cubic arrangement (*i.e.* present at all the corners of the cube)**
- **Cs^+ ions occupy cubic sites (*i.e.* occupy the centre of the cube)**
- **C.N. of Cs^+ = 8**
- **C.N. of Cl^- = 8**



Cesium chloride (CsCl)

Zinc sulphide (ZnS)

- **S^{2-} ions have *ccp* or *fcc* arrangement (*i.e.* S^{2-} ions occupy all the corners and all the face centres of the cube)**
- **Zn^{2+} ions occupy half of the tetrahedral sites**
- **C.N. of Zn^{2+} = 4**
- **C.N. of S^{2-} = 4**



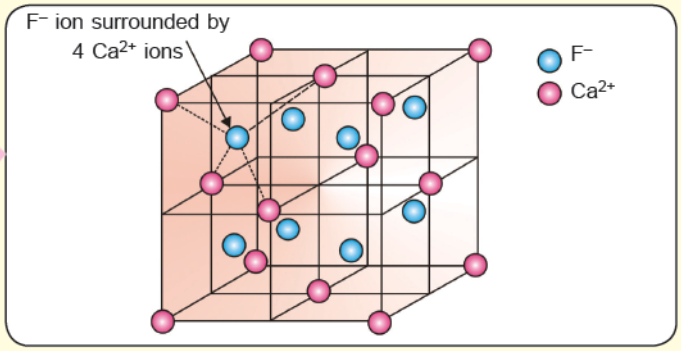
Zinc sulphide (ZnS)

- **It may be noted that ZnS exists in two forms; zinc blende and wurtzite. In zinc blende, S^{2-} ions have *ccp* or *fcc* arrangement (as shown) but in wurtzite S^{2-} ions have *hcp* arrangement. The arrangement of Zn^{2+} ions is same in both *i.e.* occupy half the tetrahedral sites.**

Calcium fluoride (CaF_2)

- **Ca^{2+} ions in ccp arrangement (*i.e.* Ca^{2+} ions occupy all the corners and all the face centres of the cube)**
- **F^- ions occupy all tetrahedral sites**
- **C.N. of Ca^{2+} = 8**
- **C.N. of F^- = 4**

- This structure is called **fluorite structure.** Sodium oxide (Na_2O) has structure reverse of fluorite structure. O^{2-} ions are arranged in ccp arrangement and Na^+ ions occupy all the tetrahedral sites. It is called **antifluorite structure**.



Calcium fluoride (CaF_2)

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Learning Plus

Structure of diamond.

Diamond has same overall geometry as zinc blende but with all atoms identical. It has face centred cubic (fcc) structure with four more atoms which are present in alternate tetrahedral voids.
There are 8 carbon atoms per unit cell in diamond as calculated below:
Diamond has 8 carbon atoms at the corners (each contributing 1/8), 6 atoms at faces (each contributing 1/2) of the cube and 4 atoms at tetrahedral sites (not shared by any other). Thus

Total number of atoms per unit cell=8 (at corners) $\times \frac{1}{8}$ + 6 (at faces) $\times \frac{1}{2}$ + 4 (at tetrahedral sites) $\times$ 1

$= 1 + 3 + 4 =$ **8 atoms**

SOLVED EXAMPLES

Example 10.

A compound is formed by two elements P and Q. Atoms of Q (as anions) make hcp lattice and those of the element P (as cations) occupy all the tetrahedral voids. What is the formula of the compound? *(Kerala S.B. 2014)*

Solution : Atoms Q adopt *hcp* arrangement and there are two tetrahedral sites per Q atom. Since all the tetrahedral sites are occupied by P atoms, this means that there are two P atoms for each Q atom.

Thus, the formula of the compound = $\mathbf{P_2Q}$.

Example 11.

Atoms of element B form hcp lattice and those of the element A occupy 2/3rd of the tetrahedral voids. What is the formula of the compound formed by these elements A and B ?

N.C.E.R.T. *(Assam S.B. 2017)*

Solution : Atoms B adopt hcp arrangement and there are two tetrahedral sites per atom of B. Since 2/3rd of the tetrahedral sites are occupied by atoms of element A, then for each atom of B, the number of A atoms will be $2 \times 2/3 = 4/3$.

Ratio of atoms A and B $= \frac{4}{3} : 1 = 4 : 3$

$\therefore$ Formula of compound : $\mathbf{A_4B_3}$.

Example 12.

In a cubic close packed structure of mixed oxides, the lattice is made up of oxide ions, one-eighth of tetrahedral voids are occupied by divalent ions (A^{2+}) while one-half of octahedral voids are occupied by trivalent ions (B^{3+}). What is the formula of the oxide ?

Solution : In a close packed arrangement, there is one octahedral and two tetrahedral voids corresponding to each atom constituting the lattice. Therefore, if

Number of oxide ions (O) per unit cell = n

Number of tetrahedral voids per oxide ion in lattice $= n \times 2 = 2n$

No. of divalent (A^{2+}) ions $= \frac{1}{8} \times 2n = \frac{n}{4}$

Number of octahedral voids per oxide ion in lattice $= n \times 1 = n$

No. of trivalent (B^{3+}) ions $= n \times \frac{1}{2} = \frac{n}{2}$

Ratio of A : B : O $= \frac{n}{4} : \frac{n}{2} : n$

or $= 1 : 2 : 4$

$\therefore$ Formula of the compound = $\mathbf{AB_2O_4}$.

Example 13.

The mineral spinel has the molecular formula Mg Al_2O_4. In this, oxide ions are present in ccp arrangement, Mg^{2+} ions occupy the tetrahedral voids while Al^{3+} ions occupy the octahedral voids. Calculate the percentage of

(i) tetrahedral voids occupied by Mg^{2+} ions
(ii) octahedral voids occupied by Al^{3+} ions.

Solution : According to the formula $MgAl_2O_4$, there are 4 oxide ions, $1Mg^{2+}$ and 2 Al^{3+} ions per formula unit. If 4 oxide ions are in *ccp* arrangement, there will be 4 octahedral voids and 8 tetrahedral voids. Thus, 1 Mg^{2+} ion is present in one of the 8 tetrahedral voids and 2 Al^{3+} ions are present in 2 octahedral voids out of 4 available.

(*i*) Percentage of tetrahedral voids occupied by Mg^{2+} ions

$= \frac{1}{8} \times 100 = 12.5\%$

(*ii*) Percentage of octahedral voids occupied by Al^{3+} ions

$= \frac{2}{4} \times 100 = 50\%$

Practice Problems

18. A solid is made of two elements X and Y. Atoms X are in fcc arrangement and Y atoms occupy all the octahedral sites and alternate tetrahedral sites. What is the formula of the compound ?

19. A compound is formed by two elements X and Y. Atoms of element Y (as anions) make ccp and those of the element X (as cations) occupy all the octahedral voids. What is the formula of the compound? ***N.C.E.R.T.***

20. A compound is formed by two elements M and N. The element N forms ccp and M atom occupy 1/3 of the tetrahedral voids. What is the formula of the compound? ***N.C.E.R.T.*** *(Pb.S.B. 2013, D.S.B. 2015)*

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21. In a crystalline solid, anions Y are arranged in ccp arrangement. Cations X are equally distributed between tetrahedral and octahedral voids. If all the octahedral voids are occupied, what is the formula of the solid ?

22. In a metallic oxide, oxide ions are arranged in cubic close packing. One sixth of the tetrahedral voids are occupied by cations P and one third of octahedral voids are occupied by the cations Q. Deduce the formula of the compound. *(Pb.S.B. 2018)*

23. In corrundum, oxide ions are arranged in *hcp* arrangement and the aluminium ions occupy 2/3 of the octahedral voids. What is the formula of corrudum ?

Answers to Practice Problems

18. XY_2. **19.** XY.
20. M_2N_3. **21.** X_2Y.
22. PQO_3. **23.** Al_2O_3.

Hints & Solutions on page 57A

Learning Plus

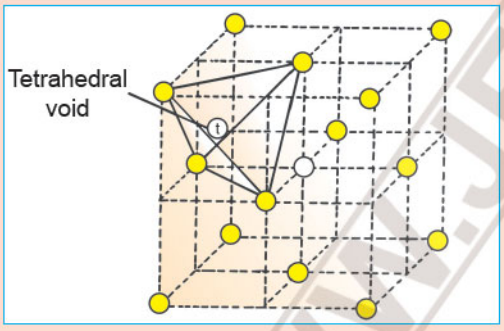
LOCATING TETRAHEDRAL AND OCTAHEDRAL VOIDS

We have learnt that close packed structures have both tetrahedral and octahedral voids. Let us visualize these voids in *ccp* (or *fcc*) structures.

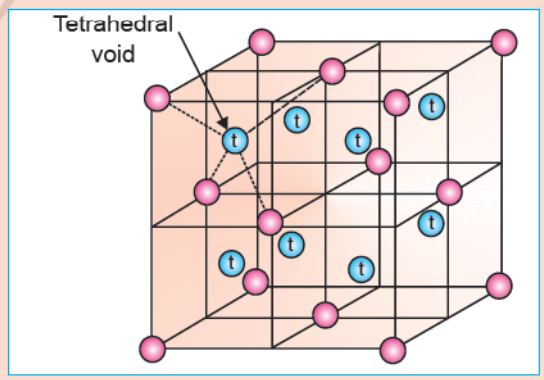
▸ Locating Tetrahedral Voids

Let us consider a unit cell of *ccp* or *fcc* lattice. It has atoms at all the corners of the cube and at the centre of each face as shown in Fig.1(*a*). If we see carefully, we observe that the unit cell has eight small cubes. Each small cube has atoms at alternate corners. Therefore, each small cube has 4 atoms. When joined to each other, they make a regular tetrahedron. **The centre of the small cube becomes tetrahedral void.** Thus, there is one tetrahedral void in each small cube. Since there are eight small cubes and therefore, there are **eight tetrahedral voids in *ccp* unit cell.**

We know that *ccp* structure has 4 atoms per unit cell. Thus, **the number of tetrahedral voids is twice the number of atoms.** In Fig. 1(*a*) only one tetrahedral site is shown while in Fig 1 (*b*) eight tetrahedral voids in *ccp* structure are shown.



(*a*) One tetrahedral void in *ccp* structure.



(*b*) Eight tetrahedral voids in *ccp* structure.

Fig.1. Locating tetrahedral voids in *ccp* structure.

▸ Locating Octahedral Voids

Let us consider the unit cell of *ccp* or *fcc* lattice. It has atoms at all the corners and at the centre of each face as shown in Fig. 2(*a*). If we carefully see, we observe that the body centre of the cube, O, is not occupied but it is surrounded by six atoms on centre of six faces. If these face centres are joined, they make an octahedron. Thus, the centre of this octahedron *i.e.*, point O becomes octahedral void.

In addition to body centre, there is an octahedral void at the centre of each edge as shown Fig. 2(*b*). It is also surrounded by six atoms as shown in Fig. 2(*b*).

Thus in a *ccp* unit cell, there are 12 octahedral voids located on edges and 1 at the body centre of the cube. Now, each edge of the cube is shared between four adjacent unit cells, so is the octahedral void located on it. This means that 1/4th of each void belongs to a particular unit cell.

Thus, in ccp structure, the number of octahedral voids are :

Octahedral void at the body centre of the cube = 1

Octahedral voids at the edges = $12 \times \frac{1}{4} = 3$

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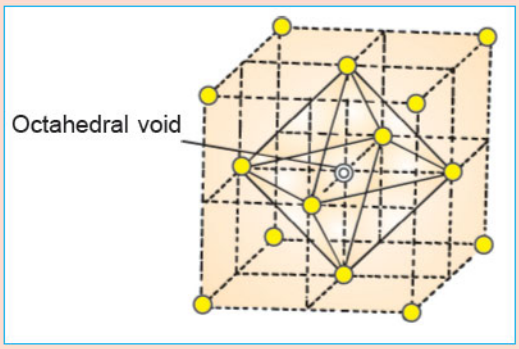
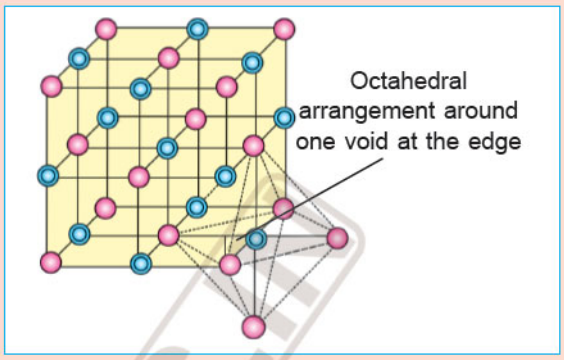
$\therefore$ Total number of octahedral voids = 1 + 3 = 4

We know that in *ccp* structure, each unit cell has 4 atoms. Therefore, **the number of octahedral voids are same as the number of atoms.**





(*a*) Octahedral void at body centre of *ccp* unit cell (*b*) 12 octahedral voids at the edges in *ccp* unit cell (shown ●)

Fig.2. Locating octahedral voids in *ccp* structure.

Advanced Levels PROBLEMS *Accelerate Your Potential (for JEE Advance)*

Problem 1. In a crystalline solid, anions Y^- are arranged in *hcp*. Cation X^+ are equally distributed between octahedral and tetrahedral voids. If all the octahedral voids are occupied, what is the formula of the compound ?

Solution Suppose the number of anions, Y^- – N

Then number of octahedral voids = N

Number of tetrahedral voids = 2N

Since octahedral and tetrahedral voids are equally occupied by cations X^+ and all the octahedral voids are occupied, then N cations X^+ are present in octahedral voids and N cations X^+ are present in tetrahedral voids. Thus,

No. of cations present = N + N = 2N

Ratio of cations and anions = 2 : 1

$\therefore$ Formula of the compound = $\mathbf{X_2Y}$.

Problem 2. In a face centred lattice of X and Y, X atoms are present at the corners while Y atoms are at face centres.

(*a*) What is the formula of the compound ?

(*b*) What would be the formula of the compound if:

(*i*) one of the X atoms is missing from a corner in each unit cell,

(*ii*) two atoms of X are missing from the corners,

(*iii*) one of the X atoms from a corner is replaced by Z atoms (also monovalent) ?

Solution (*a*) No. of X atoms in the unit cell = 8 × 1/8 = 1

No. of Y atoms in the unit cell = $6 \times \frac{1}{2} = 3$

Formula = $\mathbf{XY_3}$

(*i*) If one X atom is missing, no. of X atoms = 7/8

Formula $X_{7/8}Y_3$ or $\mathbf{X_7Y_{24}}$

(*ii*) If two X atoms are missing, no. of X atoms = 6/8 = 3/4

Formula = $X_{3/4}Y_3$ or = $\mathbf{XY_4}$

(*iii*) No. of X atoms = 7/8, No. of Z atoms = 1/8

No. of Y atoms = 3

Formula = $X_{7/8}Y_3Z_{1/8}$ or $\mathbf{X_7Y_{24}Z}$

Problem 3. In a normal spinel structure, O^{2-} ions form *fcc* packing and 1/8 of the tetrahedral sites are occupied by divalent metal, A^{2+} ions and half of the octahedral sites are occupied by trivalent metal B^{3+} ions, what is the ratio of tetrahedral/octahedral sites:

(*i*) occupied in spinel structure

(*ii*) not occupied in spinel structure

Solution Since O^{2-} ions form *fcc* structure, there will be four O^{2-} ions per unit cell. Therefore,

No. of octahedral sites = 4

No. of tetrahedral sites = 4 × 2 = 8

(*i*) No. of tetrahedral sites occupied = $8 \times \frac{1}{8} = 1$

No. of octahedral sites occupied = $4 \times \frac{1}{2} = 2$

$\therefore$ $\frac{\text{Tetrahedral sites}}{\text{Octahedral sites}} = \frac{1}{2}$ or 1 : 2

(*ii*) No. of tetrahedral sites unoccupied = 8 – 1 = 7

No. of octahedral sites unoccupied = 4 – 2 = 2

$\therefore$ $\frac{\text{Tetrahedral sites}}{\text{Octahedral sites}} = \frac{7}{2}$ or 7 : 2

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Conceptual Questions 1A

CONCEPTUAL QA

Q.1. A metal crystallizes in a body centred cubic structure. If 'a' is the edge length of its unit cell, 'r' is the radius of the sphere. What is the relationship between 'r' and 'a'? ***(CBSE Sample Paper 2017-18)***

Ans. $r = \frac{\sqrt{3}}{4} a$

Q.2. If the radius of the octahedral void is 'r' and radius of the atoms in close packing is 'R'. What is the relation between 'r' and 'R'? ***(CBSE Sample Paper 2017-18)***

Ans. $r = 0.414$ R.

Q.3. In a close packing of N spheres, how many
(*i*)tetrahedral, and (*ii*) octahedral sites are present?

Ans. (*i*) Tetrahedral = 2N, (*ii*) Octahedral = N.

Q.4. Arrange simple cubic, body centred cubic, face centred cubic and hexagonal close packing in the increasing order of packing efficiency.

Ans. Simple cubic < body centred cubic < face centred cubic = hexagonal close packing.

Q.5. (*a*) What is meant by the term coordination number ?
(*b*) What is the coordination number of atoms:
(*i*) in a cubic close packed structure (*ii*) in a body centred cubic structure ?

Ans. (*a*) Coordination number is the number of nearest neighbours of any constituent particle in the crystal lattice.
(*b*) (*i*) 12 (*ii*) 8.

Q.6. The ions of NaF and MgO all have the same number of electrons and the internuclear distances are about the same (235 pm and 215 pm). Why then are the melting points of NaF and MgO so different (992°C and 2642°C) ?

Ans. In MgO, both the ions carry two units of charge (Mg^{2+}, O^{2-}) whereas in NaF, each ion carries only one unit charge ($Na^{+}F^{-}$). Therefore, there are stronger electrostatic forces of attraction in MgO and, hence, more energy is required to overcome these forces. Thus, its melting point is high.

Q.7. Name the (*i*) most symmetrical and (*ii*) most unsymmetrical crystal system.

Ans. (*i*) Most symmetrical crystal system : Cubic
(*ii*) Most unsymmetrical crystal system : Triclinic.

Q.8. How many atoms can be assigned to its unit cell if an element forms (*i*) a body centred cubic cell and (*ii*) face centred cubic cell ? ***(A.I.S.B. 2005)***

Ans. (*i*) 2 (*ii*) 4.

Q.9. What is the maximum coordination number of an atom in a hcp crystal structure of an element.? ***(D.S.B. 2005)***

Ans. 12.

Q.10. Which network solid is an exceptionally good conductor of electricity?

Ans. Graphite, a network solid is a good conductor of electricity.

Q.11. How are unit cell and space lattice related ?

Ans. Space lattice is obtained by repeating the unit cell in three dimensions. The spatial arrangement, stoichiometry and density of unit cell and space lattice are equivalent.

Q.12. Pick out the odd ones from the following sets :
(*i*) Sulphur, Argon, Solid CO_2, Diamond ; (*ii*) SiC, Quartz, BaO, Graphite

Ans. (*i*) Diamond because all others are molecular solids.
(*ii*) BaO because all others are covalent solids.

Q.13. What is the two dimensional coordination number of a molecule in square packed layer ?
N.C.E.R.T. (Meghalaya S.B. 2017)

Ans. 4.

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CONCEPTUAL QA

Q.14. Solid A is very hard electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it ? ***N.C.E.R.T.***

Ans. Covalent or network solid like quartz (SiO_2) or SiC.

Q.15. What type of solids are electrical conductors, malleable and ductile ? ***N.C.E.R.T.***

Ans. Metallic solids.

Q.16. How many octahedral voids are there in 1 mole of a compound having cubic closed packed structure ? ***(CBSE Sample Paper 2007)***

Ans. 1 mole

Q.17. What is the total number of atoms per unit cell in a face centred cubic structure ? ***(A.I.S.B., 2008, D.S.B. 2008)***

Ans. 4.

Q.18. Some of the very old glass objects appear slightly milky instead of being transparent. Why ? ***(A.I.S.B.2007)***

Ans. This is because of some crystallization in that region.

Q.19. An ionic compound AB_2 possesses CaF_2 type crystal structure. Write the co-ordination numbers of A^{2+} and B^- ions in crystals of AB_2. ***(D.S.B. 2000)***

Ans. C. N. of $A^{2+} = 8$; C. N. of $B^- = 4$.

Q.20. An iron oxide crystallizes in a hexagonal close packed arrangement of oxide ions with two out of every three octahedral voids occupied by iron. Give the formula of the iron oxide. ***(Meghalaya S.B. 2014)***

Ans. In a close packed arrangement, there is one octahedral site corresponding to each atom constituting the lattice. Therefore,

No. of oxide ions per unit cell in hcp arrangement = 6

No. of octahedral holes = $6 \times 1 = 6$

$$\text{No. of iron ions} = 6 \times \frac{2}{3} = 4$$

Formula of the compound = Fe_4O_6 or Fe_2O_3.

Q.21. If three elements X, Y and Z crystallize in a cubic solid with X atoms at the corners, Y atoms at the cube centres and Z atoms at the faces of the cube, then write the formula of the compound.

Ans. Atom X per unit cell = $8 \times \frac{1}{8} = 1$

Atom Y per unit cell = 1

Atom Z per unit cell = $6 \times \frac{1}{2} = 3$

$\therefore$ Formula of the compound = XYZ_3

Q.22. In a solid 'AB', 'A' atoms have *ccp* arrangement and B atoms occupy all the octahedral sites. If all the face centred atoms along one of the axes are removed, then what will be the resultant stoichiometry of the compound?

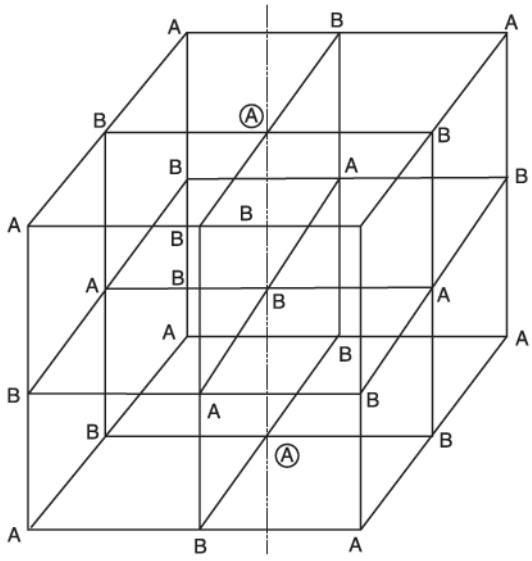
Ans. In *ccp* type structure, there are 8A at the corners of the cube and 6A atoms on the face centres. If all the face centred atoms along one of the axes are removed, it means removal of 2A atoms. Therefore, only 4 atoms will be left on faces.

$$\text{No. of A atoms per unit cell} = 8 \times \frac{1}{8} + 4 \times \frac{1}{2} = 3$$

No. of B atoms in *ccp* structure are 12 at edge centred and 1 at body centre. Therefore,

$$\text{No. of B atoms per unit cell} - 12 \times \frac{1}{4} + 1 - 4$$

$\therefore$ Stoichiometry of compound = A_3B_4.



2Ⓐatoms along one axis are removed.

Q.23. Both diamond and rhombic sulphur are covalent solids but the latter has very low melting point than the former. Explain why ?

Ans. Diamond is a network covalent solid with strong interatomic forces whereas sulphur is a molecular solid consisting of puckered eight membered rings (S_8) held together by weak van der Waals forces.

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CONCEPTUAL QA

Q.24. Write a feature which will distinguish a metallic solid from an ionic solid. ***(D.S.B. 2010)***

Ans. Metallic solids are good conductors of heat and electricity whereas ionic solids are insulators in solid state but conductors in molten state and in aqueous solution.

Q.25. Write a distinguishing feature of metallic solids. ***(A.I.S.B. 2010)***

Ans. Metallic solids are good conductors of heat and electricity.

Q.26. What is the difference between glass and quartz while both are made up from SiO_4 tetrahedra? Under what conditions could quartz be converted into glass ?

Ans. Glass is an amorphous solid while quartz is a crystalline solid. On melting quartz and then rapidly cooling *i.e.*, annealing, quartz is converted to glass.

Q.27. What difference in behaviour between the glass and sodium chloride would you expect to observe if you break off a piece of either cube ?

Ans. The glass (an amorphous solid) would break irregularly, usually in curved shapes because its component molecules are not arranged in an ordered pattern. On the other hand, sodium chloride (an ionic solid) would break off along flat surfaces parallel to the faces of the cube because the planes of its component ions are parallel to the faces of the crystalline cube.

Q.28. KF has *ccp* structure. Calculate the radius of the unit cell if the side of the cube or edge length is 400 pm. How many F^- ions and octahedral voids are there in the unit cell ? ***(CBSE Sample Paper 2011)***

Ans. For *ccp* lattice, $r = \frac{a}{2\sqrt{2}} = \frac{400}{2\times 1.414} = 141.4$ **pm**

There are four F^- ions and four octahedral voids.

Q.29. What is the relationship between the edge length *(a)* of the unit cell and radius *(r)* of an atom in a face centred unit cell? ***(Meghalaya S.B. 2013)***

Ans. $r = \frac{a}{2\sqrt{2}}$

Q.30. How will you show that glass is a supercooled liquid ?

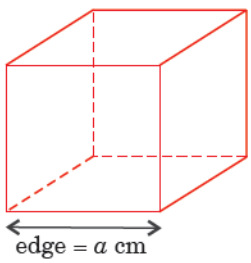
Ans. On being heated, glass has the property to flow like liquids. If we examine carefully the window panes of old buildings, we observe that they become slightly thicker at the bottom than at the top. This is because glass flows down very slowly and makes the bottom portion slightly thicker. Hence, glass is called supercooled liquid.

CALCULATIONS INVOLVING UNIT CELL DIMENSIONS

From the dimensions of the unit cell, it is possible to calculate the volume of the unit cell. From the knowledge of the density of unit cell, we can calculate the mass of atoms in the unit cell or vice-versa.

If we know the edge of a cubic crystal of an element or compound, we can easily calculate its density as described below :

Consider a unit cell of edge 'a' (cm)



The length of the edge of the cell = a cm

Volume of unit cell = a^3 cm^3

$$\text{Density of unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} \quad \ldots (i)$$

Mass of unit cell = Number of atoms in a unit cell × Mass of each atom = $Z \times m$ ... (ii)

where Z = number of atoms in unit cell and

m = mass of each atom

Mass of an atom present in unit cell,

$$m = \frac{\text{Atomic mass}}{\text{Avogadro number}} = \frac{M}{N_A}$$

$$\text{Mass of unit cell} = Z \times \frac{M}{N_A}$$

Substituting in eq. (i), we get

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A} \text{ g cm}^{-3}$$

If edge length 'a' is in pm, then

Edge length = a pm

$= a \times 10^{-12}$ m $= a \times 10^{-10}$ cm

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Volume of unit cell = $(a \times 10^{-10}\ cm)^3$
$= a^3 \times 10^{-30}\ cm^3$

So, the formula becomes

$$\text{Density of unit cell} = \frac{Z \times M}{a^3 \times 10^{-30} \times N_A}\ g\ cm^{-3}$$

where 'a' is in pm.
In terms of SI units, if a is in metres and M is in kg mol^{-1}, then

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}\ kg\ m^{-3}$$

Density of unit cell is the same as the density of the substance. If the density of the element is known by other method, Avogadro number or number of atoms in a given amount of element can be easily calculated.

The density of solids can be used in different ways.

NOTE

It may be noted that the relation considers the cubic crystals of elements. However, for cubic crystals of ionic compounds, the formula is the same except that in the case of ionic compounds, Z is the number of formula units present in one unit cell and M is formula mass.

Solving Numerical Problems

KEY FORMULAE AND UNITS

Density of unit cell (and hence density of a crystal),

$$\rho = \frac{Z \times M}{a^3 \times N_A}$$

where a is edge of unit cell in **cm**
N_A = Avogadro number (6.022×10^{23})
M = Atomic mass of element or formula mass of the compound.
Z = No. of atoms present per unit cell or formula units
e.g. for *fcc*, Z = 4,
for bcc, Z = 2,
for simple cubic, Z = 1.

SOLVED EXAMPLES

A. Unit Cell Dimensions and Density

Example 14.

An element having bcc geometry has atomic mass 50u. Calculate the density of the unit cell, if its edge length is 290 pm.
(Mizoram S.B. 2015, Pb. S.B. 2015, 2016)

Solution : Length of edge, a = 290 pm
$= 290 \times 10^{-10}$ cm

Since it is *bcc* arrangement,

No. of atoms in the unit cell, Z = 2

Atomic mass of the element, M = 50 g mol^{-1}

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$$= \frac{2 \times 50\ g\ mol^{-1}}{(290 \times 10^{-10}\ cm)^3 \times (6.022 \times 10^{23}\ mol^{-1})}$$

$$= \mathbf{6.81\ g\ cm^{-3}}.$$

Example 15.

Copper crystallizes with face centred cubic unit cell. If the radius of copper atom is 127.8 pm, calculate the density of copper metal. (Atomic mass of Cu = 63.55 u and Avogadro's number, $N_A = 6.02 \times 10^{23}$ mol^{-1}). *(A.I.S.B. 2012)*

Solution : For a *fcc* unit cell, edge length (a) is related to radius of atom as :

$$r = \frac{a}{2\sqrt{2}}$$

or $a = 2\sqrt{2}.r = 2 \times 1.414 \times 127.8$
$= 361.42$ pm
or $= 361.42 \times 10^{-10}$ cm

Since the lattice is *fcc*, the number of copper atoms per unit cell, $Z = 4$.

$$\text{Density, } \rho = \frac{Z \times M}{a^3 \times N_A}$$

M = 63.55 u, $N_A = 6.02 \times 10^{23}$

$$\therefore \quad \rho = \frac{4 \times 63.55}{(361.42 \times 10^{-10})^3 \times (6.02 \times 10^{23})}$$

$$= \mathbf{8.94\ g\ cm^{-3}}$$

Example 16.

Sodium has body centred cubic structure having nearest neighbour distance 365.9 pm. Calculate its density. (Atomic mass of sodium = 23 g mol^{-1}.)

Solution : For the *bcc* structure, edge length is related to nearest neighbour distance (d) as

$$d = \frac{\sqrt{3}}{2}a \quad \text{or} \quad a = \frac{2d}{\sqrt{3}}$$

$$\therefore \quad a = \frac{2 \times 365.9}{1.732} = 422.5\ pm = 422.5 \times 10^{-10}\ cm$$

$$\text{Density, } \rho = \frac{Z \times M}{a^3 \times N_A}$$

Z = 2 (for *bcc*), M = 23 g mol^{-1}, $N_A = 6.02 \times 10^{23}$

$$\therefore \ \rho = \frac{2 \times 23}{(422.5 \times 10^{-10})^3 \times (6.02 \times 10^{23})} = \mathbf{1.01 g\ cm^{-3}}$$

Example 17.

An element crystallizes in a fcc lattice with cell edge of 250 pm. Calculate its density if 300 g of this element contain 2×10^{24} atoms. (D.S.B. 2016)

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Solution : Length of edge, $a = 250 \text{ pm} = 250 \times 10^{-12} \text{ m}$
$= 250 \times 10^{-10} \text{ cm}$

Volume of unit cell $= (250 \times 10^{-10} \text{ cm})^3$
$= 15.625 \times 10^{-24} \text{ cm}^3$

Mass of unit cell = No. of atoms in unit cell × Mass of each atom

Since the element has fcc arrangement, the number of atoms per unit cell, $Z = 4$

$$\text{Mass of an atom} = \frac{300}{2\times10^{24}} \text{ g}$$

$$\therefore \text{Mass of unit cell} = \frac{300}{2\times10^{24}} \times 4 = 6.0 \times 10^{-22} \text{ g}$$

$$\text{Density of unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{6.0\times10^{-22} \text{ g}}{15.625\times10^{-24} \text{ cm}^3}$$

$$= \mathbf{38.4 \text{ g cm}^{-3}}$$

❑ Example 18.

A metal having atomic mass 50 g mol^{-1} has a body centred cubic crystal structure. The density of metal is 5.96 g cm^{-3}. Find the volume of the unit cell.

(H.P.S.B. 2001, Pb S.B. 2016 Mizoram S.B. 2013, 2018)

Solution : If a is the edge length of the unit cell, then volume of unit cell, $V = a^3$

Density of unit cell, $\rho = 5.96 \text{ g cm}^{-3}$

Atomic mass of the metal, $M = 50 \text{ g mol}^{-1}$

No. of atoms per unit cell, $Z = 2$ (*bcc*)

Now, $$\text{Density} = \frac{Z\times M}{a^3\times N_A}$$

or $$\rho = \frac{Z\times M}{V\times N_A}$$

or $$V = \frac{Z\times M}{\rho\times N_A}$$

$$\therefore \text{Volume} = \frac{2\times(50 \text{ g mol}^{-1})}{(5.96 \text{ g cm}^{-3})\times(6.022\times10^{23} \text{ mol}^{-1})}$$

$$= \mathbf{27.86 \times 10^{-24} \text{ cm}^3.}$$

B. Lattice Type from Density and Unit Cell Dimensions

❑ Example 19.

The density of chromium metal is 7.2 g cm^{-3}. If the unit cell is cubic with edge length of 289 pm, determine the type of unit cell (simple, body centred or face centred) [Atomic mass of Cr = 52 a.m.u., $N_A = 6.02 \times 10^{23}$ mol^{-1}]. (Pb. S. B. 2014, 2017)

Solution : Length of the edge = 289 pm = 289×10^{-12} m = 289×10^{-10} cm

Atomic mass of Cr, $A = 52 \text{ g mol}^{-1}$

Density of metal, $\rho = 7.2 \text{ g cm}^{-3}$

Now, $$\rho = \frac{Z\times M}{a^3\times N_A}$$

$$7.2 \text{ g cm}^{-3} = \frac{Z\times 52 \text{ g mol}^{-1}}{(289\times10^{-10}\text{cm})^3\times(6.022\times10^{23}\text{mol}^{-1})}$$

or $$Z = \frac{(7.2 \text{ g cm}^{-3})\times(289\times10^{-10}\text{cm})^3\times(6.022\times10^{23}\text{mol}^{-1})}{(52 \text{ g mol}^{-1})}$$

$$= \mathbf{2.01}$$

Since the unit cell contains 2 atoms, it is **body centred cubic (*bcc*).**

❑ Example 20.

An element with molar mass 27 g mol^{-1} forms a cubic unit cell with edge length 4.05 × 10^{-8} cm. If its density is 2.7 g cm^{-3}, what is the nature of the unit cell ? *(D.S.B. 2015)*

Solution : Density of unit cell, $\rho = \frac{Z\times M}{a^3\times N_A}$

$\rho = 2.7 \text{ g cm}^{-3}$, $a = 4.05 \times 10^{-8}$ cm, $M = 27 \text{ g mol}^{-1}$, $N_A = 6.022 \times 10^{23}$

$$\therefore \quad 2.7 = \frac{Z\times 27}{(4.05\times10^{-8})^3\times6.022\times10^{23}}$$

or $$Z = \frac{2.7\times(4.05\times10^{-8})^3\times6.022\times10^{23}}{27} = 4.0$$

Since $Z = 4$, the unit cell is face centred cubic (*fcc*) unit cell.

C. Atomic Mass and Number of Atoms from Density and Unit Cell Dimensions

❑ Example 21.

An element with density 11.2 g cm^{-3} forms a fcc lattice with edge length of 4 × 10^{-8} cm. Calculate the atomic mass of the element.

(D. S. B. 2014, Pb. S.B. 2016)

Solution : Edge length of the unit cell

$a = 4 \times 10^{-8}$ cm

Density $= 11.2 \text{ g cm}^{-3}$

No. of atoms per unit cell in *fcc* lattice, $Z = 4$

Density, $$\rho = \frac{Z\times M}{a^3\times N_A}$$

$$11.2 \text{ g cm}^{-3} = \frac{4\times M}{(4\times10^{-8}\text{cm})^3\times(6.02\times10^{23}\text{mol}^{-1})}$$

or $$M = \frac{(11.2\text{g cm}^{-3})\times(4\times10^{-8}\text{ cm})^3\times(6.02\times10^{23}\text{ mol}^{-1})}{4}$$

$$= 107.9 \text{ g mol}^{-1}$$

Atomic mass of element **= 107.9 u.**

❑ Example 22.

An element has a body centred cubic (bcc) structure with a cell edge of 288 pm. The density of the element is 7.2 g cm^{-3}. How many atoms are present in 208 g of the element ? *(D.S.B. 2006, Pb.S.B. 2007)*

Solution : Edge length of the unit cell = 288 pm
$= 288 \times 10^{-10}$ cm

Volume of the unit cell $= (288 \times 10^{-10})^3 \text{ cm}^3$
$= 2.39 \times 10^{-23} \text{ cm}^3$

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Mass of element = 208 g

Density of element = 7.2 g cm^{-3}

$$\text{Volume of 208 g of the element} = \frac{\text{Mass}}{\text{Density}}$$

$$\text{Volume of element} = \frac{208\text{ g}}{7.2\text{ g cm}^{-3}} = 28.89\text{ cm}^3$$

Number of unit cells in this volume

$$= \frac{\text{Volume of element}}{\text{Volume of unit cell}}$$

$$= \frac{28.89\text{ cm}^3}{2.39\times10^{-23}\text{cm}^{-3}\text{ / unit cell}}$$

$$= 12.08 \times 10^{23}\text{ unit cells}$$

Since the structure is *bcc*, number of atoms present in a unit cell = 2

The number of atoms in 208 g of the element

$$= 2 \times 12.08 \times 10^{23} = 24.16 \times 10^{23}\text{ atoms}$$

or $$= \mathbf{2.416 \times 10^{24}\text{ atoms}}$$

❑ Example 23.

An element E crystallizes in body centred cubic structure. If the edge length of the cell is 1.469 × 10^{-10} m and the density is 19.3 g cm^{-3}, calculate the atomic mass of this element. Also calculate the radius of an atom of the element.

(CBSE Sample Paper 2007)

Solution : Edge length of the unit cell, $a = 1.469 \times 10^{-10}$ m = 1.469×10^{-8} cm

Density, ρ = 19.3 g cm^{-3}

Since it is body centred, Z = 2

$$\rho = \frac{Z\times M}{a^3\times N_A}$$

$$19.3\text{ g cm}^{-3} = \frac{2\times M}{(1.469\times10^{-8}\text{cm})^3\times(6.022\times10^{23}\text{ mol}^{-1})}$$

$$\text{or } M = \frac{(19.3\text{ g cm}^{-3})\times(1.469\times10^{-8}\text{cm})^3\times(6.022\times10^{23}\text{ mol}^{-1})}{2}$$

$$= 18.42\text{ g mol}^{-1}$$

∴ Atomic mass = **18.42** u.

For a *bcc* structure, radius of an atom,

$$r = \frac{\sqrt{3}}{4}\cdot a = \frac{1.732\times1.469\times10^{-10}\text{m}}{4}$$

$$= \mathbf{6.36 \times 10^{-11}\text{ m}}$$

D. The Avogadro Constant from Density and Unit Cell Dimensions

❑ Example 24.

Calculate the value of Avogadro number from the following data :

Density of NaCl = 2.165 g cm^{-3}, distance between Na^+ and Cl^- ions in NaCl crystal = 281 pm.

(A.I.S.B. 2004, H.P.S.B. 2005, Pb. S.B. 2011, Hr. S.B. 2017 Nagaland S.B. 2018)

Solution : Sodium chloride has face centred cubic structure. Therefore, the number of formula units or molecules per unit cell, Z = 4

Let Avogadro number = N_A

Molar mass of NaCl = 23 + 35.5 = 58.5 g mol^{-1}

Since distance between Na^+ and Cl^- ions is 281 pm, the length of edge is double the distance between Na^+ and Cl^- ions.

Edge of unit cell = 2 × 281 pm = 562 pm

or = 562 × 10^{-12} m = 562 × 10^{-10} cm

Density, $$\rho = \frac{Z\times M}{a^3\times N_A}$$

$$2.165\text{ g cm}^{-3} = \frac{4\times(58.5\text{ g mol}^{-1})}{(562\times10^{-10}\text{cm})^3\times N_A}$$

or $$N_A = \frac{4\times(58.5\text{ g mol}^{-1})}{(2.165\text{ g cm}^{-3})\times(562\times10^{-10}\text{cm})^3}$$

$$= \mathbf{6.09 \times 10^{23}\text{ mol}^{-1}.}$$

E. Unit Cell Dimensions and Ionic Radii from Density

❑ Example 25.

The compound CuCl has fcc structure like ZnS. Its density is 3.4 g cm^{-3}. What is the length of the edge of the unit cell ? *(Mizoram S.B. 2014)*

Solution : CuCl has cubic close packed or face centred cubic structure like ZnS. The number of formula units or molecules of CuCl per unit cell = 4.

Let length of each edge = a cm

∴ Volume of the cube = a^3 cm^3

Density of the cell = 3.4 g cm^{-3}

Formula mass of CuCl, M = 63.5 + 35.5 = 99

Density $$\rho = \frac{Z\times M}{a^3\times N_A}$$

$$3.4\text{ g cm}^{-3} = \frac{4\times(99\text{ g mol}^{-1})}{a^3\times(6.022\times10^{23}\text{mol}^{-1})}$$

or $$a^3 = \frac{4\times(99\text{ g mol}^{-1})}{(3.4\text{ g cm}^{-3})\times(6.022\times10^{23}\text{mol}^{-1})}$$

$$= 193.4 \times 10^{-24}\text{ cm}^3$$

∴ $$a = \mathbf{5.78 \times 10^{-8}\text{ cm or 578 pm.}}$$

❑ Example 26.

An element A crystallises in fcc structure. 200 g of this element has 4.12×10^{24} atoms. The density of A is 7.2 g cm^{-3}. Calculate the edge length of the unit cell. *(A.I.S.B. 2001)*

Solution : Let length of each edge = a cm

Volume of unit cell = a^3 cm^3

Density = 7.2 g cm^{-3}

$$\text{Mass of each atom} = \frac{200}{4.12\times10^{24}}$$

$$= 48.54 \times 10^{-24}\text{ g}$$

No. of atoms per unit cell = 4 (*fcc*)

Mass of unit cell = $4 \times 48.54 \times 10^{-24}$

$$= 194.16 \times 10^{-24}\text{ g}$$

$$\text{Now, density} = \frac{\text{Mass}}{\text{Volume}}$$

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$$7.2 = \frac{194.16\times10^{-24}}{a}$$

or $$a^3 = \frac{194.16\times10^{-24}}{7.2} = 26.97\times10^{-24}\ cm^3$$

or $$a = \mathbf{2.999\times10^{-8}\ cm = 299.9\ pm.}$$

❑ Example 27.

Niobium crystallizes in body centered cubic structure. If density is 8.55 g cm^{-3}, calculate atomic radius of niobium given its atomic mass 93 u.

N.C.E.R.T.

Solution : Density = 8.55 g cm^{-3}

Let length of the edge = a cm

Number of atoms per unit cell, Z = 2 *(bcc)*

Atomic mass, M = 93 g mol^{-1}

Density, $$\rho = \frac{Z\times M}{a^3\times N_A}$$

$$8.55\ g\ cm^{-3} = \frac{2\times(93\ g\ mol^{-1})}{a^3\times(6.022\times10^{23}\ mol^{-1})}$$

$$\therefore\quad a^3 = \frac{2\times(93\ g\ mol^{-1})}{(8.55\ g\ cm^{-3})\times(6.022\times10^{23}\ mol^{-1})}$$

$$= 36.12\times10^{-24}\ cm^3$$

Edge length, $a = (36.12\times10^{-24})^{1/3} = 3.306\times10^{-8}$ cm

$$= 3.306\times10^{-10}\ m$$

Now, radius in body centred cubic, $r = \frac{\sqrt{3}}{4}a$

$$= \frac{\sqrt{3}\times3.306\times10^{-10}\ m}{4} = 1.431\times10^{-10}\ m$$

$$= \mathbf{0.143\ nm.}$$

❑ Example 28.

KF has NaCl structure. What is the distance between K$^+$ and F$^-$ in KF if density is 2.48 g cm^{-3} ?

(Hr. S.B. 2005)

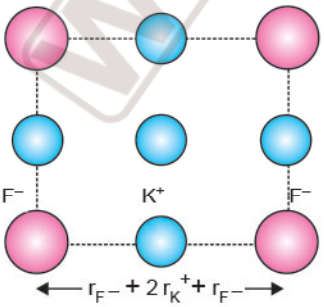
Solution : KF has NaCl *(fcc)* structure, therefore, the number of KF molecules per unit cell, Z = 4

Molar mass of KF = 58 g mol^{-1}

Let the edge of unit cell = a cm

Density, ρ = 2.48 g cm^{-3}

Density, $$\rho = \frac{Z\times M}{a^3\times N_A}$$



$$2.48\ g\ cm^{-3} = \frac{4\times58\ g\ mol^{-1}}{a^3\times(6.022\times10^{23}\ mol^{-1})}$$

$$a^3 = \frac{4\times58\ g\ mol^{-1}}{(2.48\ g\ cm^{-3})\times(6.022\times10^{23}\ mol^{-1})}$$

$$= 155.3\times10^{-24}\ cm^3$$

$$\therefore\quad a = (155.3\times10^{-24})^{1/3}$$

or $a = 5.375\times10^{-10}$ cm or 537.5 pm

Now, if radius of F$^-$ is r_{F^-} and radius of K$^+$ is r_{K^+}, then according to the figure, edge of unit cell,

$$a = r_{F^-} + 2r_{K^+} + r_{F^-}$$

$$= 2(r_{K^+} + r_{F^-})$$

or $$r_{K^+} + r_{F^-} = \frac{a}{2}$$

Thus, distance between K$^+$ and F$^-$ ions will be half the edge length in the unit cell.

Thus, the distance between K$^+$ and F$^-$ ions = $\frac{537.5}{2}$

$$= \mathbf{268.8\ pm.}$$

❑ Example 29.

Aluminium crystallizes in a cubic close packed structure. Its metallic radius is 125 pm.

(a) What is the length of the side of unit cell?

(b) How many unit cells are there in 1.00 cm^3 of Al ?

(D.S.B. 2005, A.I.S.B. 2005, Meghalaya S.B. 2018)

Solution : For a cubic close packed structure, length of the side of unit cell is related to radius.

$$r = \frac{a}{2\sqrt{2}}$$

or $$a = r\times2\sqrt{2}$$

$$= 125\times2\times1.414\ pm = 353.5\ pm$$

Volume of unit cell = $(353.5\times10^{-10}\ cm)^3 = 4.42\times10^{-23}\ cm^3$

No. of unit cells in 1 cm^3 = $\frac{1}{4.42\times10^{-23}}$

$$= \mathbf{2.26\times10^{22}\ unit\ cells.}$$

❑ Example 30.

Silver has atomic mass 108 a.m.u. and density 10.5 g cm^{-3}. If the edge length of its unit cell is 409 pm, identify the type of unit cell. Also calculate the radius of an atom of silver.

Solution : Edge length of unit cell

$$a = 409\ pm$$

$$= 409\times10^{-10}\ cm$$

Density, ρ = 10.5 g cm^{-3}

Atomic mass of silver = 108 u

Now, $$\rho = \frac{Z\times M}{a^3\times N_A}$$

$$10.5\ g\ cm^{-3} = \frac{Z\times(108\ g\ mol^{-1})}{(409\times10^{-10}\ cm)^3\times(6.022\times10^{23}\ mol^{-1})}$$

or $$Z = \frac{(10.5\ g\ cm^{-3})\times(409\times10^{-10}\ cm)^3\times(6.022\times10^{23}\ mol^{-1})}{108\ g\ mol^{-1}}$$

Z = 4.0

Since the unit cell contains 4 atoms per unit cell, it is **face centred cubic** *(fcc)* unit cell.

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For *fcc*, $r = \frac{a}{2\sqrt{2}} = \frac{409\,\text{pm}}{2\times1.414} = \mathbf{144.6\,pm}$

❑ Example 31.

Silver metal crystallises with a face centred cubic lattice. The length of the unit cell is found to be 4.077 × 10⁻⁸ cm. Calculate atomic radius and density of silver. (Atomic mass of Ag = 108u, N_A = 6.02 × 10²³ mol⁻¹).

(C.B.S.E. Sample Paper 2012, H.P.S.B. 2016)

Solution : Edge length of unit cell, $a = 4.077 \times 10^{-8}$ cm

For *fcc* lattice, radius of an atom is related to edge length, a as :

$$r = \frac{a}{2\sqrt{2}} = \frac{4.077\times10^{-8}}{2\times1.414} = \mathbf{1.441\ \ 10^{-8}\ cm}$$

$$\text{Density, } \rho = \frac{Z\times M}{a^3\times N_A}$$

$$= \frac{4\times108}{(4.077\times10^{-8})^3\times(6.02\times10^{23})} \quad (\because Z = 4 \text{ for } fcc)$$

$$= \mathbf{10.58\ g\ cm^{-3}}$$

❑ Example 32.

The density of lead is 11.35 g cm⁻³ and the metal crystallizes with fcc unit cell. Estimate the radius of lead atom. (At. Mass of lead = 207 g mol⁻¹ and N_A = 6.02 × 10²³ mol⁻¹) *(D.S.B. 2011)*

Solution : Let length of edge = a cm

Density = 11.35 g cm⁻³

No. of atoms per unit cell in *fcc* lattice = 4

Atomic mass, M = 207 g mol⁻¹

$$\text{Density, } \rho = \frac{Z\times M}{a^3\times N_A}$$

$$11.35\ \text{g cm}^{-3} = \frac{4\times(207\ \text{g mol}^{-1})}{a^3\times(6.022\times10^{23}\,\text{mol}^{-1})}$$

$$a^3 = \frac{4\times(207\ \text{g mol}^{-1})}{(11.35\ \text{g cm}^{-3})\times(6.022\times10^{23}\,\text{mol}^{-1})} = 121.14\times10^{-24}\ \text{cm}^3$$

Edge length, $a = (121.14)^{1/3}\times10^{-8} = 4.948\times10^{-8}$ cm

or $= 4.948\times10^{-10}$ m

or $= 494.8\times10^{-12}$ m = 494.8 pm

Now, radius in *fcc* $= \frac{a}{2\sqrt{2}} = \frac{494.8\ \text{pm}}{2\times1.414} = \mathbf{174.96\ pm}$

Practice Problems

24. An element 'X' (At. mass = 40 g mol⁻¹) having f.c.c. structure, has unit cell edge length of 400 pm. Calculate the density of 'X' and the number of unit cells in 4 g of 'X'. (N_A = 6.022 × 10²³ mol⁻¹) *(A.I.S.B. 2018)*

25. An element crystallizes in a f.c.c. lattice with cell edge of 400 pm. The density of the element is 7 g cm⁻³. How many atoms are present in 280 g of the element? *(A.I.S.B. 2016)*

26. Tungsten has body centred cubic lattice. Each edge of the unit cell is 316 pm and density of the metal is 19.35 g cm⁻³. How many atoms are present in 50 g of the element ? *(Pb.S.B. 2011)*

27. CsCl has body centred cubic lattice with the length of a side of a unit cell 412.1 pm and aluminium is face centred cubic lattice with length of the side of unit cell 405 pm. Which of the two has larger density ? (Atomic mass of Cs = 132.9, Al = 26.9, Cl = 35.5)

28. Unit cell of an element (atomic mass = 108 amu and density = 10.5 g cm⁻³) has edge length 409 pm. Deduce the type of the crystal lattice. *(Nagaland S.B. 2016, Pb.S.B.2017)*

29. Iron has a body centred cubic unit cell with a cell dimension of 286.65 pm. The density of iron is 7.874 g cm⁻³. Use this information to calculate Avogadro number. (At. mass of Fe = 55.845 u) *(A.I.S.B. 2009; D.S.B. 2009)*

30. Gold (atomic mass = 197 u, atomic radius = 0.144 nm) crystallizes in a face centred unit cell. Determine the density of gold, (N_A = 6.022 × 10²³ mol⁻¹). *(C.B.S.E. Sample Paper 2010)*

31. An element (atomic mass = 60) having face centred cubic structure has a density of 6.23 g cm⁻³. What is the edge length of the unit cell ? *(Pb.S.B. 2015)*

32. An element with density 10 g cm⁻³ forms a cubic unit cell with edge length of 3 × 10⁻⁸ cm. What is the nature of the cubic unit cell if the atomic mass of the element is 81 g mol⁻¹ ? *(A.I.S.B. 2015)*

33. Lead (II) sulphide crystal has NaCl structure. What is its density ? The edge length of the unit cell of PbS crystal is 500 pm. (atomic masses : Pb = 207, S = 32) *(Pb.S.B. 2008)*

34. Formula mass of NaCl is 58.45 g mol⁻¹ and density of its pure form is 2.167 g cm⁻³. The average distance between adjacent sodium and chloride ions in the crystal is 2.814 × 10⁻⁸ cm. Calculate the Avogadro number.

Answers to Practice Problems

24. 4.15 g cm⁻³, 1.505 × 10²²
25. 2.5 × 10²⁴ atoms
26. 1.64 × 10²³ atoms.
27. Density of CsCl = 3.995 g cm⁻³, density of Al = 2.69 g cm⁻³. CsCl has larger density.
28. Z = 4, *fcc*
29. 6.022 ×× 10²³
30. 19.41 g cm⁻³
31. 400 pm
32. *bcc*
33. 12.7 g cm⁻³ **34.** 6.06 × 10²³

Hints & Solutions on page 57A

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35. Copper crystallizes into a *fcc* lattice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3}.

36. Crystalline CsBr has a cubic structure. Calculate the unit cell edge length if the density of CsBr crystal is 4.24 g cm^{-3} (atomic masses : Cs = 133, Br = 80).

37. The unit cell of an element of atomic mass 108 and density 10.5 g cm^{-3} is a cube with edge length of 409 pm. Find the structure of the crystal lattice (simple cube, *fcc* or *bcc*). Avogadro's number = 6.023×10^{23}.

(Pb. S.B. 2014, Meghalaya S.B. 2015)

38. What is the distance between Na^+ and Cl^- ions in NaCl crystal if the density is 2.165 g cm^{-3}. Molar mass of NaCl = 58.5 g mol^{-1}, ($N_A = 6.02 \times 10^{23}$ mol^{-1}.) *(A.I.S.B. 2006)*

39. A compound AB crystallizes in bcc lattice with unit cell edge length of 380 pm. Calculate

(*i*) the distance between oppositely charged ions in the lattice.

(*ii*) radius of A^+ if radius of B^- is 175 pm.

40. Thallium chloride TlCl crystallises in either a simple cubic lattice or a face centred cubic lattice of Cl^- ions with Tl^+ ions in the holes. If the density of the solid is 7.00 g cm^{-3} and edge of the unit cell is 3.85×10^{-8} cm, what is the unit cell geometry ? (Atomic mass of Tl = 208.37 and of Cl = 35.5).

41. Cesium chloride crystallizes as cubic lattice and has a density of 4.0 g cm^{-3}. Calculate the length of the edge of the unit cell of cesium chloride. (Molar mass of CsCl = 168.5 g mol^{-1}) *(D.S.B. 2003)*

42. An element having atomic mass 107.9 u has FCC lattice. The edge length of its unit cell is 408.6 pm Calculate density of the unit cell. [Given, $N_A = 6.022 \times 10^{23}$ mol^{-1}] *(Karnataka S.B. 2018)*

43. Calculate the Avogadro number from the following data of AB when AB has NaCl type structure :

Density of AB = 2.48 g cm^{-3}, M = 58

Distance between A^+ and B^- ions in AB = 269 pm

(Hr.S.B. 2005)

44. X-ray diffraction studies show that copper crystallizes in a fcc unit cell with cell edge of 3.61×10^{-8} cm. In a separate experiment copper is determined to have a density of 8.92 g cm^{-3}. Calculate the molar mass of copper. *(H.P.S.B. 2005)*

45. Chromium crystallizes in a body centred cubic lattice whose density is 7.20 g/ cm^3. The length of the edge of unit cell is 288.4 pm. Calculate the Avogadro number (atomic mass of chromium = 52).

(Pb S.B. 2013, Meghalaya S.B. 2016)

46. An element has atomic mass 93 g mol^{-1} and density 11.5 g cm^{-3}. If the edge length of its unit cell is 300 pm, identify the type of unit cell. *(D.S.B. 2017)*

Answers to Practice Problems

35. 8.96 g cm^{-3}

36. 436.9 pm.

37. *fcc* type

38. 282 pm

39. (*i*) 329.1 pm

(*ii*) 154.1 pm

40. Z = 1. Simple cubic.

41. 412 pm

42. 10.506 g cm^{-3}

43. 6.007×10^{23}.

44. 63.2. g mol^{-1}

45. 6.02×10^{23}

46. *bcc*

Hints & Solutions on page 57A

Advanced Levels PROBLEMS *Accelerate Your Potential (for JEE Advance)*

Problem 4. Lithium borohydride ($LiBH_4$) crystallizes in an orthorhombic system having 4 molecules per unit cell. The unit cell dimensions are: $a = 6.81$ Å, $b = 4.43$ Å and $c = 7.17$ Å. Calculate the density of the crystal (At. mass of Li = 7, B = 11, H = 1u).

Solution Since orthorhombic unit cell has all the angles, $\alpha = \beta = \gamma = 90°$, then

Volume of unit cell $= a \times b \times c$

Molar mass of $LiBH_4$ $= 7 + 11 + 4 \times 1 = 22$ g mol^{-1}.

$$\rho = \frac{Z \times M}{(a \times b \times c) N_A}$$

$$= \frac{4 \times (22 \text{ g mol}^{-1})}{6.81 \times 10^{-8} \times 4.43 \times 10^{-8} \times 7.17 \times 10^{-8} \text{ cm}^3) \times (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$= 0.676 \text{ g cm}^{-3}$$

Problem 5. Iron crystallizes in several forms. At 1185 K, the body centred cubic α-form of iron changes to the face centred cubic γ-form of iron. Assuming that the distance between the nearest neighbours is the same in two forms at the transition temperature, calculate the ratio of the density of α-form to that of γ-form at the transition temperature.

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Solution For body centred α-form

$$r = \frac{\sqrt{3}}{4}a \quad \text{or} \quad a = \frac{4r}{\sqrt{3}}$$

No. of atoms of per unit cell, Z = 2

$$\text{Density of } \alpha\text{-form of iron} = \frac{Z \times M}{N_A \times a^3} = \frac{2 \times M}{N_A \times (4r/\sqrt{3})^3}$$

For face centred γ-form, $r = \frac{a}{2\sqrt{2}}$ or $a = 2\sqrt{2}\, r$

No. of atoms of per unit cell, Z = 4

$$\text{Density of } \gamma\text{-form of iron} = \frac{Z \times M}{N_A \times a^3} = \frac{4 \times M}{N_A \times (2\sqrt{2}\, r)^3}$$

$$\frac{\text{Density of } \alpha\text{-form of iron}}{\text{Density of } \gamma\text{-form of iron}} = \frac{2}{(4r/\sqrt{3})^3} \times \frac{(2\sqrt{2}r)^3}{4}$$

$$= \frac{2 \times 3\sqrt{3} \times 16\sqrt{2}}{64 \times 4}$$

$$= \frac{3 \times 1.732 \times 1.414}{8} = \mathbf{0.918}$$

Problem 6. KCl and NaCl crystallize in the same form and $\frac{r_{Na^+}}{r_{Cl^-}} = 0.52$ and $\frac{r_{Na^+}}{r_{K^+}} = 0.71$

Calculate

(*i*) ratio of the side of the unit cell for KCl to that for NaCl.

(*ii*) the ratio of density of KCl to that of NaCl.

Solution (*i*) Both KCl and NaCl crystallize in face centred cubic arrangement in which the face length is related to radii of cation and anion as:

$$r_{Na^+} + r_{Cl^-} = \frac{a}{2} \quad \text{and} \quad r_{K^+} + r_{Cl^-} = \frac{a'}{2}$$

Now $$\frac{r_{Na^+}}{r_{Cl^-}} = 0.52$$

or $$\frac{r_{Na^+}}{r_{Cl^-}} + 1 = 0.52 + 1$$ (adding 1 on both sides)

or $$\frac{r_{Na^+} + r_{Cl^-}}{r_{Cl^-}} = 1.52 \quad \ldots(i)$$

$$\frac{r_{Na^+}}{r_{K^+}} = 0.71$$

But $$r_{Na^+} = r_{Cl^-} \times 0.52 = 0.52\, r_{Cl^-}$$

$$\therefore \quad \frac{0.52\, r_{Cl^-}}{r_{K^+}} = 0.71$$

or $$\frac{r_{K^+}}{r_{Cl^-}} = \frac{0.52}{0.71}$$

$$\frac{r_{K^+}}{r_{Cl^-}} + 1 = \frac{0.52}{0.71} + 1$$

$$\frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} = \frac{0.52 + 0.71}{0.71} = \frac{1.23}{0.71} \quad \ldots(ii)$$

Dividing eq. (*ii*) by eq. (*i*)

$$\frac{r_{K^+} + r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = \frac{1.23}{0.71} \times \frac{1}{1.52}$$

or $$\frac{\frac{a'}{2}}{\frac{a}{2}} = 1.14$$

$$\therefore \quad \frac{\text{Side of unit cell for KCl}}{\text{Side of unit cell for NaCl}} = 1.14$$

(*ii*) $$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

Since Z and N_A are same for both KCl and NaCl

$$\text{Density} \propto \frac{M}{a^3}$$

$$\therefore \quad \frac{\rho(KCl)}{\rho(NaCl)} = \frac{M(KCl)}{M(NaCl)} \times \frac{[a(NaCl)]^3}{[a(KCl)]^3}$$

$$= \frac{74.5}{58.5} \times \left(\frac{1}{1.14}\right)^3 \quad \left(\because \frac{a(NaCl)}{a(KCl)} = \frac{1}{1.14}\right)$$

$$= \mathbf{0.86}$$

IMPERFECTIONS IN SOLIDS

Crystalline solids are formed by regular repetition of large number of unit cells in all directions. **An ionic crystal which has the same unit cell containing the same lattice points throughout the whole of crystal** is known as **ideal crystal.** However, such ideal crystals exist only at absolute zero (0 K) temperature. At any temperature above 0 K, the crystals have some departure from complete ordered arrangement. In actual practice, it is very difficult to grow a perfect or an ideal crystal. A solid consists of a number of many small individual crystals or grains, each of which is deformed because it is highly packed among other deformed crystals. Even single crystals which are grown with all care and which appear to be perfect may contain some internal irregularities.

Any deviation from completely ordered arrangement of constituent particles in a crystal *is called* ***disorder or a defect.***

The crystal may have additional defects due to the presence of some impurities. The term **disorder** or **imperfection** is generally used to denote departure from perfectly ordered state of the constituents of the crystals. These imperfections will not only change the properties of the crystals but also give rise to new properties.

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TYPES OF DEFECTS

Broadly speaking, there are two types of defects:

(*i*) *Point defects* (*ii*) *Line defects*

(i) Point defects

The defects which arise due to the irregularity or deviations from ideal arrangement of atoms around a point or an atom in a crystalline substance are called **point defects or atomic imperfections.**

(ii) Line defects

The defects which arise due to irregularities or deviations from ideal arrangement in entire row of lattice points are called **line defects.**

These irregularities are called **crystal defects or crystal imperfections**. In the present unit we shall confine our discussion to point defects only.

POINT DEFECTS IN SOLIDS

The point defects arise due to any one of the following causes :

(*i*) Vacancy defect. *When some of the lattice sites are vacant, the crystal is said* to have **vacancy defect** (Fig. 39). The unoccupied positions are called vacancies. This defect results in decrease in density of the substance. This type of defect may also develop when a substance is heated and therefore, it is also called **thermodynamic defect.**

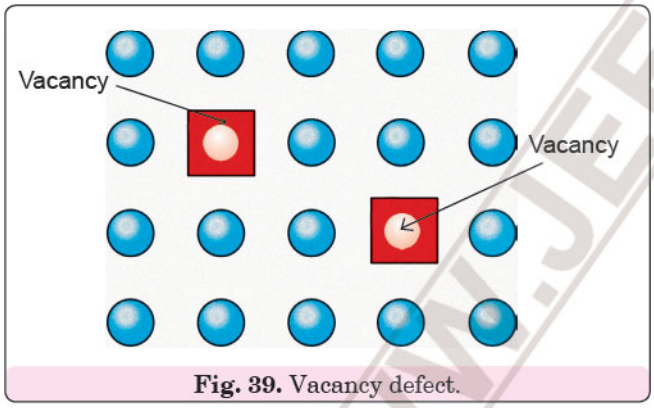

Fig. 39. Vacancy defect.

(*ii*) Interstitial defect. *When some constituent particles (atoms or molecules) occupy vacant interstitial positions, the crystal is said to have* ***interstitial defect*** (Fig. 40). This defect increases the density slightly.

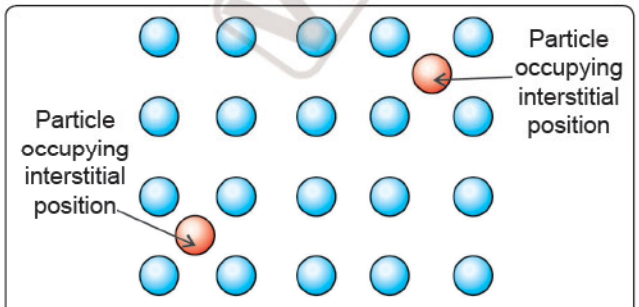

Fig. 40. Interstitial defect.

It may be noted that vacancy and interstitial defects are shown by non-ionic solids. On the otherhand, ionic solids must always maintain electrical neutrality.

The **point defects** in ionic crystals may be classified as:

A. *Defects in stoichiometric crystals.*

B. *Defects in non-stoichiometric crystals.*

C. *Impurity defects*

A. Point Defects in Stoichiometric Crystals

Stoichiometric compounds *are those in which the number of positive and negative ions are exactly in the ratios indicated by their chemical formulae.* For simplicity, we can consider the compounds of the type AB having equal number of A^+ and B^- ions. The defects in these types of compounds are called **stoichiometric defects**. In these compounds two types of defects are generally observed. These are :

1. *Schottky defect.* 2. *Frenkel defect.*

1. Schottky defect

This defect was discovered by German scientist Schottky in 1930. *It arises if some of the atoms or ions are missing from their normal lattice sites.* The lattice sites which are unoccupied are called **lattice vacancies** or **holes.** Since the crystal is to remain electrically neutral, equal number of cations and anions are missing. The ideal AB crystal is shown in Fig. 41. The existence of two holes one due to a missing cation and the other due to a missing anion is shown in Fig. 42. This is basically a vacancy defect in ionic solids.

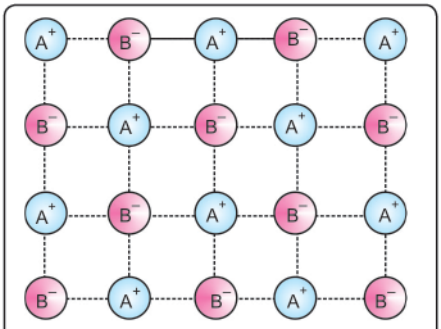

Fig. 41. An ideal crystal.

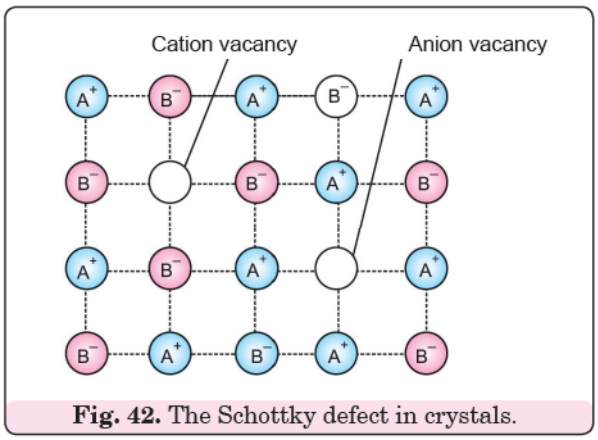

Fig. 42. The Schottky defect in crystals.

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Conditions causing Schottky defects. This type of defect is usually observed in strongly ionic compounds having

(*i*) *high co-ordination number, and*

(*ii*) *ions (cations and anions) of almost similar sizes.*

For example, NaCl, KCl, KBr, CsCl and AgBr ionic solids have Schottky defects. It has been observed that in NaCl, there are about 10^6 Schottky pairs per cm^3 at room temperature. In one cm^3, there are about 10^{22} ions and this means that there will be one Schottky defect per 10^{16} ions in NaCl. Because of the presence of large number of vacancies in crystals, **its density is markedly lowered**.

2. Frenkel defect

This defect was discovered by a Russian scientist Frenkel in 1926. *It arises when an ion is missing from its normal position (causing a vacancy or a hole) and occupies an interstitial site between the lattice points.* The existence of one hole due to a missing cation from its normal position and occupying an interstitial position is shown in Fig. 43. In this case also, the crystal remains electrically neutral because the number of anions and cations remains the same.

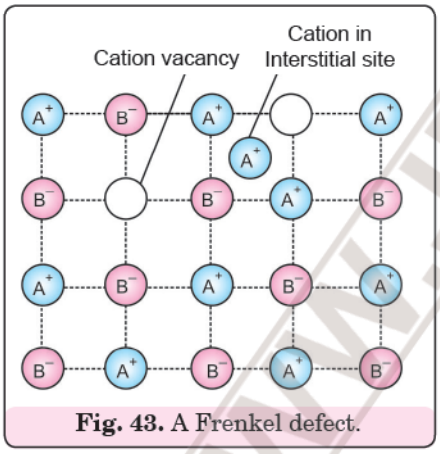

Fig. 43. A Frenkel defect.

This defect is also known as **interstitial defect.** It creates a *vacancy defect* at its original position and an *interstitial defect* in its new location.

Conditions causing Frenkel defects. This defect generally occurs in compounds in which

(*i*) *co-ordination number is low,*

(*ii*) *anions are much larger in size than the cations.*

In pure alkali metal halides, these defects are not very common because the ions cannot get into interstitial positions due to their large sizes. These defects can be found in silver halides such as AgCl, AgBr, AgI, ZnS, etc. Because of the small size of the Ag^+ ion and Zn^{2+} ion, these ions can go into the interstitial sites.

We observe that vacancies or holes are present in crystals with Schottky as well as Frenkel defect *but the former leads to decrease in the overall density of the substance but the latter does not.*

It may be noted that in addition to two basic types of defects (Schottky and Frenkel), another hybrid type of defect can also arise from a combination of the two.

Consequences of Schottky and Frenkel Defects. Schottky and Frenkel defects in crystals lead to some *interesting consequences.* These are given below :

1. Because of the presence of these defects, the electrical conductivity of crystals increases. When an electric field is applied, a nearby ion moves from its lattice site to occupy a 'hole'. This results in creating a new 'hole' and another nearby ion moves into it and so on. This process continues and a hole, thereby, moves from one end to the another end. Thus, it conducts electricity across the whole of the crystal.

2. Due to the presence of holes in the crystal, its density decreases. However, it may be noted that density decreases only for crystals having Schottky defects.

3. The presence of 'holes' also decreases *the lattice energy or the stability of the crystal.* The presence of too many holes may cause a partial collapse of the lattice.

4. The closeness of similar charges in Frenkel defects tends *to increase the dielectric constant of the crystals.*

NOTE

It may be noted that in certain ionic solids such as AgBr, both Schottky and Frenkel defects occur.

Differences between Schottky and Frenkel Defects

Schottky defect	Frenkel defect
1. It is produced because of missing atoms or ions from their normal crystal sites.	It is produced when some atoms or ions are displaced from their normal sites and occupy interstitial sites.
2. The presence of Schottky defect lowers the density of the crystal.	It does not affect the density of the crystal.
3. It is generally shown by ionic solids having high co-ordination number and in which cations and anions are of equal sizes *e.g.,* NaCl, CsCl.	It is generally exhibited by ionic solids having low co-ordination number and in which anions are larger in size than cations *e.g.,* AgCl, ZnS.

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B. Point Defects in Non-Stoichiometric Crystals

The compounds in which the ratio of positive and negative ions present in the compound differs from that required by ideal chemical formula of the compound are called **non-stoichiometric compounds**.* The defects in these compounds are called **non-stoichiometric defects**. Vanadium oxide, for example has, the formula VO_x where x lies between 0.6 and 1.3. Similarly, iron (II) oxide of ideal composition FeO are difficult to obtain. Normally, we get samples of more oxygen atoms than iron atoms (composition of $Fe_{0.95}$ O but it may range from $Fe_{0.93}$ O to $Fe_{0.96}$ O). ZnO usually has excess of zinc atoms than oxygen atoms, ZnO_x ($x < 1$). However, it may be noted that in each case, the electrical neutrality of the crystal is maintained. Non-stoichiometric behaviour is most commonly found for transition metal compounds. It is also found for some lanthanoids and actinoids.

These are of two types depending upon whether positive ions are in excess or negative ions are in excess. These are also known as **metal excess defects** and **metal deficiency defects** respectively. Some of these examples are given below :

(A) Metal Excess Defects

In these defects, the positive ions are in excess. These may arise due to the following two ways :

(*i*) anionic vacancies

(*ii*) presence of extra cations in interstitial sites.

(*i*) Anion vacancies. In this case, *negative ions may be missing from their lattice sites leaving holes in which the electrons remain entrapped to maintain the electrical neutrality*. This is shown in Fig. 44. Evidently, there is an excess of positive (metal) ions although, the crystal as a whole is electrically neutral. This type of defect is observed in those crystals which are likely to form Schottky defects.

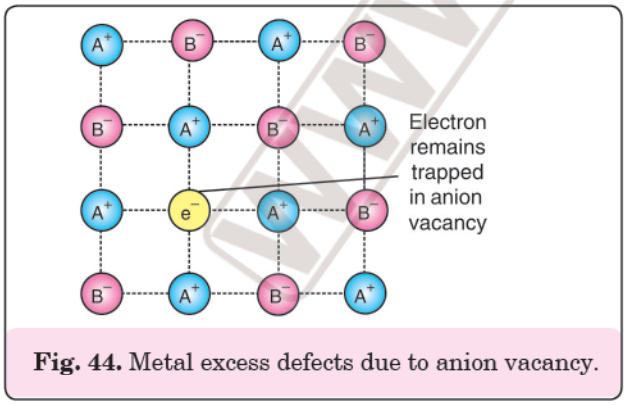

Fig. 44. Metal excess defects due to anion vacancy.

In alkali metal halides, anion vacancies are produced when alkali metal halide crystals are heated in the atmosphere of the alkali metal vapours. For example, when crystal of NaCl are heated in an atmosphere of sodium vapour, the excess of sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by the loss of electrons by sodium atoms to form Na^+ ions. The electrons, thus produced by the ionisation of the sodium atoms diffuse into the crystal and get trapped at the anion vacancies. The electrons trapped in anion vacancies are referred to as **F-centres** (from German word *farbenzenter* meaning colour centre). They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of potassium in KCl makes the crystal appear violet (or lilac), excess of lithium in LiCl makes the crystal appear pink.

NOTE

The electrons trapped in anion vacancies are called **F-centres** because they impart colour to crystals.

(*ii*) Excess cations occupying interstitial sites. In this case, *there are extra positive ions occupying interstitial sites and the electrons in another interstitial sites to maintain electrical neutrality*. This is shown in Fig. 45. The defect may be visualised as the loss of non-metal atoms which leave their electrons behind. The excess metal ions occupy interstitial positions.

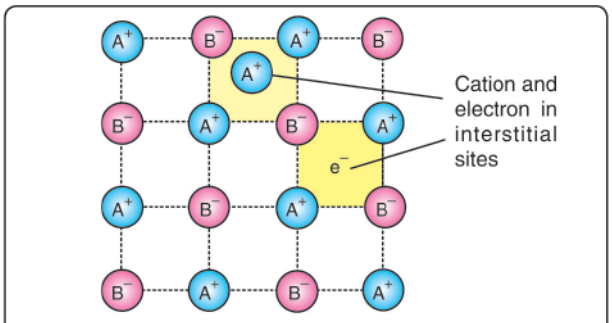

Fig. 45. Metal excess defects due to extra cation.

This type of defect is found in crystals which are likely to develop Frenkel defect. The common example is zinc oxide. Zinc oxide (ZnO) is white in colour at room temperature. On heating, it loses oxygen reversibly at high temperatures and turns yellow in colour.

$$ZnO \xrightarrow{\text{Heat}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

The excess Zn^{2+} ions are trapped in interstitial sites and equal number of electrons are trapped in the neighbourhood to balance the electrical charge. These electrons give rise to enhanced electrical conductivity.

* Non-stoichiometric compounds are sometimes called **berthollides** after the name of French inorganic chemist Claude Louis Berthollet, who studied such compounds.

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Consequences of Metal Excess Defects

1. *The crystals with metal excess defects conduct electricity due to the presence of free electrons.* However, the conductivity is very low because of the number of defects and therefore, the number of free electrons is very small. Because of low conductivity as compared to conductivity of metals, these are called semiconductors. These compounds are also called ***n*-type semi-conductors** since the current is carried by the electrons in the normal way.

2. The crystals with metal excess defects are generally coloured. For example, *non-stoichiometric sodium chloride is yellow, non-stoichiometric potassium chloride is violet.*

(B) Metal Deficient Defects

These contain less number of positive ions than negative ions. These arise due to two ways :

(*i*) *Cation vacancies*

(*ii*) *Extra anions occupying interstitial sites*

(*i*) **Cation vacancies.** In some cases, *the positive ions may be missing from their lattice sites. The extra negative charge may be balanced by some nearby metal ion acquiring two positive charges instead of one.* This is shown in Fig. 46.

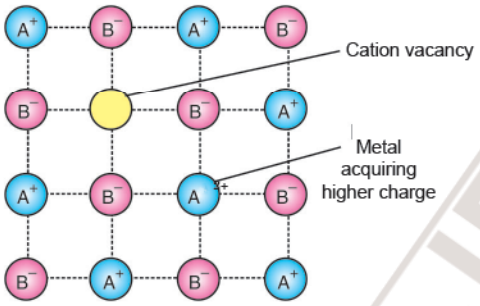

Fig. 46. Metal deficient defect due to cation vacancy.

This type of defect is possible in metals which show variable oxidation states. The common examples of compounds having this defect are ferrous oxide, ferrous sulphide, nickel oxide etc. In case of iron pyrites (FeS), for example, two out of three ferrous ions in a lattice may be converted into Fe^{3+} state and the third Fe^{2+} ion may be missing from its lattice site. Therefore, the crystal contains Fe^{2+} and Fe^{3+} ions. This gives rise to exchange of electrons from one Fe^{2+} ion to Fe^{3+} ion in which Fe^{2+} changes to Fe^{3+} and Fe^{3+} changes to Fe^{2+} ion. As a result, the crystal has metallic lustre. Because of the natural colour of iron pyrites and metallic lustre some samples of minerals shine like gold and have been nick-named as ***fool's gold***. Similarly, FeO is mostly found with a composition of $Fe_{0.95}O$. It may actually range from $Fe_{0.93}O$ to $Fe_{0.96}O$. In crystals of FeO, some Fe^{2+} ions are missing and the loss of positive charge is made up by presence of required number of Fe^{3+} ions. Moreover, since there is exchange of electrons, the substances become conductors.

REMEMBER

Because of metallic lustre of some minerals of iron pyrites, they shine like gold and have been nick named as **fool's gold**.

(*ii*) **Extra anions occupying interstitial sites.** In this case, *the extra anions may be occupying interstitial positions. The extra negative charge is balanced by the extra charges (oxidation of equal number of cations to higher oxidation states) on the adjacent metal ions.* This is shown in Fig. 47. Such type of defect is not common because the negative ions are usually very large and they cannot easily fit into the interstitial sites.

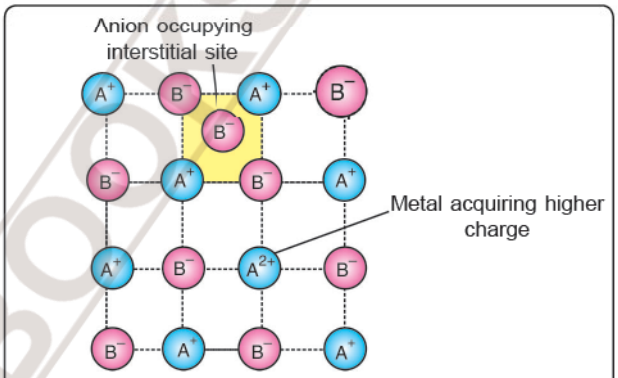

Fig. 47. Metal deficient defect due to extra anion.

Consequences of Metal Deficient Defects

Crystals with metal deficient defects are semiconductors. The conductivity is due to the movement of electron from one ion to another. For example, when an electron moves from ion A^+, it changes to A^{2+}. It is also called movement of positive hole and the substances are called ***p*-type semiconductors.**

(C) Impurity Defects

These defects in ionic crystals arise due to the presence of some impurity ions at the lattice sites (in place of host ions) or at the vacant interstitial sites. For example, if molten NaCl containing a little

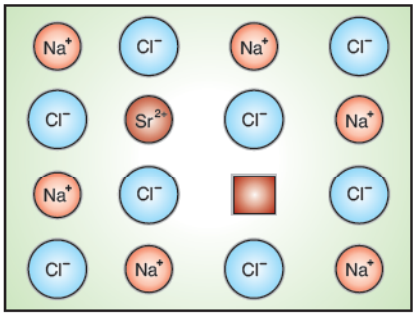

Fig. 48. Introduction of a cation vacancy in NaCl by substitution of Na^+ by Sr^{2+}.

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amount of $SrCl_2$ is allowed to crystallise, some of the sites of Na^+ ions are occupied by Sr^{2+} ions. For each Sr^{2+} ion introduced, two Na^+ ions are removed to maintain electrical neutrality. One of these lattice site is occupied by Sr^{2+} ion and the other remains vacant. This is shown in Fig. 48. Therefore, these vacancies result in increased electrical conductivity of the solid. Similar defect and behaviour is observed when $CdCl_2$ is added to AgCl.

SOLVED EXAMPLES

❑ Example 33.

If NaCl is doped with 10^{-3} mol% of $SrCl_2$, what is the concentration of cation vacancy ? **N.C.E.R.T.**

Solution : One cation of Sr^{2+} would create one cation vacancy in NaCl. Therefore, the number of cation vacancies created in the lattice of NaCl is equal to the number of divalent Sr^{2+} ions added.

∴ Concentration of cation vacancy on being doped with 10^{-3} mol % $SrCl_2$

$$= 10^{-3} \text{ mol\%} = \frac{10^{-3}}{100} = 10^{-5} \text{ mol}$$

No. of Sr^{2+} ions in 10^{-5} mol $= 10^{-5} \times 6.023 \times 10^{23}$

$= 6.023 \times 10^{18}$ Sr^{2+} ions

No. of cation vacancies = **6.023×10^{18}.**

❑ Example 34.

Analysis shows that nickel oxide has the formula $Ni_{0.98}O_{1.00}$. What fractions of the nickel exist as Ni^{2+} and Ni^{3+} ions in given oxide?

N.C.E.R.T. *(Pb.S.B. 2018)*

Solution : $Ni_{0.98}O_{1.0}$.

Let Ni^{2+} be x so that Ni^{3+} will be $0.98 - x$. Total charge on the compound must be zero so that

$$+2x + 3(0.98 - x) - 2 = 0$$

$$2x + 2.94 - 3x - 2 = 0$$

$$-x = -0.94$$

or $$x = 0.94$$

$$\% \text{ of } Ni^{2+} = \frac{0.94}{0.98} \times 100 = 96\%$$

$$\% \text{ of } Ni^{3+} = 4\%$$

❑ Example 35.

If Al^{3+} replaces Na^+ ion at the edge centre of NaCl lattice then calculate the vacancies in 1 mole of NaCl.

Solution : 1 mol of NaCl contains 1 mol of Na^+ ions *i.e.* 6.022×10^{23} Na^+ ions.

NaCl has *fcc* arrangement of Cl^- ions and Na^+ are present at the edge centres and body centres.

Since there are 12 edges and each edge is shared by 4 unit cells, then contribution of Cl^- ions present at the edge centres is $\frac{1}{4} \times 12 = 3$. Contribution of Na^+ ion present at the body centre = 1

Thus, for every 4 Na^+ ions, the ions present at the edge centres= 3.

∴ The Na^+ ions which have been replaced by Al^{3+} ions

$$= \frac{3}{4} \times 6.022 \times 10^{23} = 4.5165 \times 10^{23}$$

To maintain electrical neutrality, 1 Al^{3+} ion will replace 3 Na^+ ions. This means that 1 position will be occupied and remaining 2 will be vacant.

∴ No. of vacancies in 1 mole of NaCl

$$= \frac{2}{3} \times 4.5165 \times 10^{23} = \mathbf{3.011 \times 10^{23}}$$

Practice Problems

47. The composition of a sample of wustite is $Fe_{0.93}O_{1.00}$. What mass percentage of iron is present in the form of Fe(III) ions ?

48. Analysis shows that a metal oxide has the empirical formula $M_{0.96}O_{1.00}$. Calculate the percentage of M^{2+} and M^{3+} ions in the crystal.

(C.B.S.E. Sample Paper 2007)

Answers to Practice Problems

47. 11.5% **48.** 91.67, 8.33

Hints & Solutions on page 57A

Advanced Levels PROBLEMS *Accelerate Your Potential (for JEE Advance)*

Problem 7. A metal crystallizes in a face centred cubic unit cell with $a = 0.560$ nm. Calculate the density of the metal if it contains 0.1% Schottky defects. (Atomic mass of metal = 40 g mol^{-1})

Solution Due to Schottky defect, the vacant spaces will increase resulting decrease in number of atoms per unit cell.

In this case, $Z = \left(4 - \frac{4 \times 0.1}{100}\right) = 3.996$

Density, $\rho = \frac{Z \times M}{N_A \times a^3}$

$$= \frac{3.996 \times (40 \text{ g mol}^{-1})}{(0.560 \times 10^{-7} \text{ cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$= \mathbf{1.51 \text{ g cm}^{-3}}$$

Problem 8. By X-ray diffraction method, the unit cell edge length of sodium chloride is found to be 562.6 pm. The density of NaCl is observed to be 2.158 g cm^{-3}.

***(i)* Predict the type of defect present in the crystal.**

***(ii)* Calculate the percentage of Na^+ and Cl^- ions missing.**

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Solution (*i*) The density can be calculated as

$$\rho = \frac{Z \times M}{a^3 \times N_A}$$

$Z = 4$ (*fcc*), $M = 23 + 35.5 = 58.5$ g mol^{-1},
$a = 562.6$ pm or $= 562.6 \times 10^{-10}$ cm, $N_A = 6.022 \times 10^{23}$

$$\therefore \quad \rho = \frac{4 \times 58.5}{(562.6 \times 10^{-10})^3 \times (6.022 \times 10^{23})}$$
$$= 2.182 \text{ g cm}^{-3}$$

Observed density $= 2.158$ g cm^{-3}

Since observed density is less than theoretically calculated value, this means that some Na^+ and Cl^- ions are missing from their lattice sites *i.e.* the crystal has **Schottky defect.**

(*ii*) Actual formula units of NaCl per unit cell can be calculated as :

$$Z = \frac{a^3 \times N_A \times \rho}{M}$$

$$= \frac{(562.6 \times 10^{-10} \text{cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times (2.158 \text{ g cm}^{-3})}{(58.5 \text{ g mol}^{-1})}$$

$= 3.956$

Formula units missing per unit cell
$= 4 - 3.956 = 0.044$

$$\therefore \quad \% \text{ missing unit cells} = \frac{0.044}{4} \times 100 = \mathbf{1.1\%}$$

PROPERTIES OF SOLIDS

There is a close relationship between the properties of a solid and its composition and structure. Some important properties of solids are discussed below :

1. Electrical Properties of Solids

Solids exhibit an interesting range of variation of electrical conductivities extending over 27 orders of magnitude ranging from 10^{-20} to 10^7 ohm^{-1} m^{-1}, which no other physical property show.

On the basis of electrical conductivity, solids can be classified into three types :

(i) conductors

(ii) insulators

(iii) semiconductors.

(*i*) **Conductors.** *The solids which allow the passage of electric current* are called **conductors**. They have conductivities in the range 10^4 to 10^7 ohm^{-1} m^{-1}. For example, metals have conductivities of the order of 10^7 ohm^{-1} m^{-1} and hence are the best conductors of electricity. Conductors are of two types : *metallic conductors or electrolytic conductors.*

(*a*) **Metallic conductors** *are those which allow the electricity to pass through them without undergoing any chemical change.* For example, copper, silver etc. Metals conduct electricity in solid as well as in molten state. In metallic conductors, the conductance is due to the movement of electrons under the influence of an applied electric potential. The streams of electrons constitute the current. *The conductivity of metals depends upon the number of valence electrons available per atom.*

(*b*) **Electrolytic conductors** *are those which allow the electricity to pass through them by undergoing chemical change*. The conduction in ionic solids is due to the migration of ions or other charged particles under the applied field. Due to strong electrostatic forces of attraction, the ionic solids do not conduct electricity. However, these conduct electricity to a good extent when they are in their molten state or in the form of their aqueous solutions. In these states, the ions of the electrolyte become free and they conduct electricity due to the movement of ions.

REMEMBER

- Metals conduct electricity through the movement of electrons.
- Electrolytes conduct electricity due to movement of ions.
- Metals conduct electricity in the solid as well as molten state.
- Electrolytes conduct electricity only in aqueous solution or molten state.

(*ii*) **Insulators.** *The solids which do not allow the passage of electric current through them* are called **insulators**. They have very very low conductivities ranging between 10^{-20} to 10^{-10} ohm^{-1} m^{-1}. For example, wood, sulphur, phosphorus, rubber etc.

(*iii*) **Semiconductors.** *The solids whose conductivity lies between those of typical metallic conductors and insulators* are called **semiconductors**. The semiconductors have conductivity in the range of 10^{-6} to 10^4 Ω^{-1} m^{-1}. The conductivity of semiconductors is due to the presence of impurities and defects.

REMEMBER

Range of conductivity

- Conductors : 10^4 to 10^7 ohm^{-1}m^{-1}
- Semiconductors : 10^{-6} to 10^4 ohm^{-1}m^{-1}
- Insulators : 10^{-20} to 10^{-10} ohm^{-1}m^{-1}

Effect of Temperature on Conductivity

In general, with increase in temperature the conductivity of metals decreases while that of

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semiconductors increases. However, there is very little increase in the conductivity of an insulator as the temperature is increased.

REMEMBER

With increase in temperature electrical conductivity of
- metals decreases
- semiconductors increases.

The electrical behaviour of some typical transition metal oxides as metals (M), insulators (I) and oxides showing transition from metal to insulators behaviour (T) at a certain temperature are given below :

TiO (M)	VO (T)		MnO(I)	FeO(I)	CoO(I) NiO(I) CuO(I)
Ti_2O_3 (T)	V_2O_3 (T)	Cr_2O_3(I)	Mn_2O_3 (I)	Fe_2O_3(I)	
	VO_2 (T)	CrO_2 (M)	MnO_2 (I)		
TiO_2 (I)	V_2O_5 (I)				

Similar behaviour is exhibited by sulphides.

Learning Plus

It is very interesting to note that transition metal monoxides (MO), all of which have similar NaCl structures show very marked differences in their electrical properties.

- TiO is metallic, MnO, FeO, CuO, etc. are insulators while VO is metallic or insulator depending upon temperature.
- CrO_2 is metallic, MnO_2 is insulator while VO_2 is metallic or insulator depending upon temperature.
- ReO_3 is metallic, while VO_3 and TiO_3 are metallic or insulator depending upon temperature.

▶ Thus, transition metal oxides show marked differences in electrical properties.

To sum up

❒ TiO, CrO_2, ReO_3 are metallic.

❒ MnO, FeO, CuO, are insulators

❒ VO, VO_2, V_2O_3, TiO_3 etc. change from metallic to insulator at a certain temperature.

❒ **Rhenium oxide, ReO_3 has appearance as well as conductivity like copper.**

Mechanism of Electrical Conduction

The conduction in most of the solids is through electron movement under an electric field.However, in some ionic solids, the conduction is by ions. Therefore, in the solids where the conduction is by the movement of electrons, the electrical conductivity depends on the number of electrons available to participate in the conduction process. *The difference in electrical conductance behaviour of conductors, insulators and semiconductors* can be explained with the help of **band model.**

BAND THEORY FOR EXPLAINING THE BEHAVIOUR OF METAL CONDUCTORS, SEMICONDUCTORS AND INSULATORS

The bonding in metals can be explained by extending the simple molecular orbital theory to metals, called **band theory.** The basis of band theory is that a metal lattice has an extremely large number of atoms. The atomic orbitals of these metal atoms overlap to form a large number of molecular orbitals which are so close in energy to each other that they form **energy bands.**

Let us consider an example of lithium metal. Ignoring inner 1*s*-electrons which do not involve in bonding, 2*s*-orbitals of lithium atoms may combine to form molecular orbitals. We have learnt that in case of Li_2 (two atoms) 2*s* AOs on two lithium atoms combine to give two MOs; one bonding MO and one anti-bonding MO [Fig. 49 (*a*)]. If we have three lithium atoms, three 2*s* AOs would combine to form three MOs; one bonding, one antibonding and one non-bonding [Fig. 49 (b)].

The energy of non-bonding MO is in between the bonding and antibonding MO, exactly at the same level as the energy of the AOs. Similarly, in case of four lithium atoms, four 2*s* AOs would combine to form four MOs; two bonding and two antibonding MOs [Fig. 49 (*c*)]. Similarly, if we have N atoms of lithium (N is Avogadro number, 6.02×10^{23} atoms), 2*s* AOs of N atoms would combine to give N MOs. As the number of molecular orbitals is large, the energy levels of MOs are so close together, that they may almost be treated as continuous. Such a group of energy levels is known as **energy band** and is responsible for the name **band model for metals.**

The energy levels in a band is equal to the number of atoms in the metal. The formation of an energy band depends upon :

(*i*) the close proximity of large number of atoms.

(*ii*) the energy difference between the pure atomic orbitals.

Thus, 2*s*-atomic orbitals give rise to one energy band, the 2*p*-atomic orbitals also form a band of closely spaced energy levels. The various energy bands from different atomic orbitals may overlap or be separated from each other depending upon the relative energies of the atomic energy levels.

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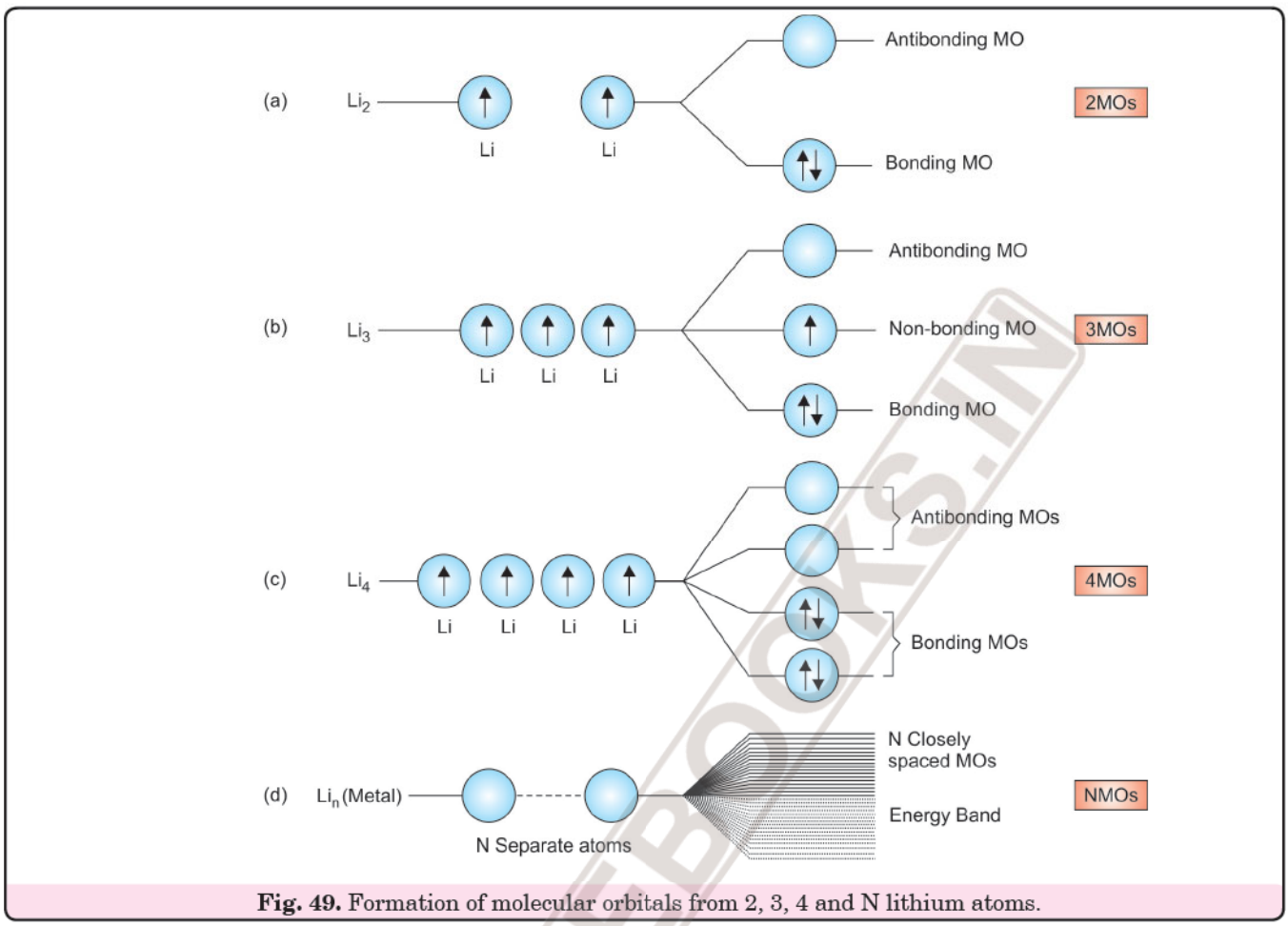

Fig. 49. Formation of molecular orbitals from 2, 3, 4 and N lithium atoms.

The energy bands formed by the overlap of 1*s*, 2*s* and 2*p* AOs of lithium metal are shown in Fig. 50.

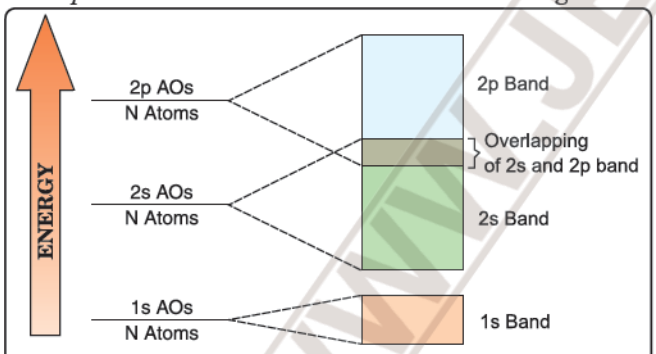

Fig. 50. Formation of energy bands in lithium atoms.

The arrangement of electrons in different energy bands determine the characteristics of a metal. Now, in the case of Li atom, the electronic configuration is $1s^2\ 2s^1$. The 1*s* energy band will be completely filled. These electrons do not contribute towards bonding and may be ignored. As already learnt, in case of Li_2, there will be 2 valence electrons and there are two MOs. Since each MO can accommodate two electrons (Pauli's exclusion principle), only bonding molecular orbital will be completely filled. Similarly, in case of Li_4, the four valence electrons would occupy only the two lowest bonding MOs.

Thus, in these cases, half of the molecular orbitals remain unoccupied. Similarly, N 2*s* atomic orbitals give N 2*s* molecular orbitals (energy band). Since Li atom has only one valence electron, only half of the molecular orbitals will be filled. In other words, only one half of the 2*s* band, will be filled in the lithium metal. This is shown in Fig. 51. (It may be noted that the bands are displaced laterally for clarity). Thus, there are many empty levels into which electrons can move. This movement of electrons from one level to another *constitutes an electric current.*

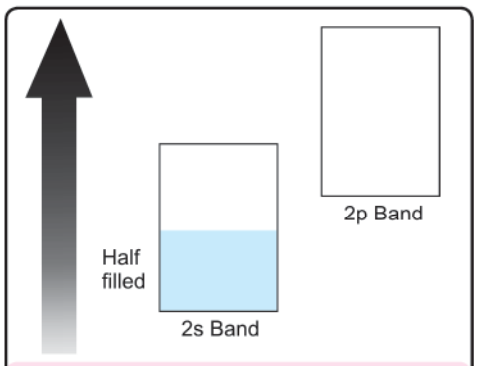

Fig. 51. The band structure for Li metal.

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Thus, lithium is good conductor. At the same time, if we heat one end of metal, electrons at that end gain energy and move to empty energy bands where they can travel easily to another part of the metal. This accounts for thermal conduction of metals.

We can apply the same arguments to beryllium. In beryllium, there are two valence electrons and therefore, N atoms of beryllium will have 2N electrons from 2*s* AOs. Therefore, in beryllium metal, the 2*s* band will be completely filled (Fig 52) There are no empty orbitals in 2*s* energy band into which electrons can move. However, 2*p* energy band is completely empty and it overlaps the 2*s* energy band. When some electric field is applied, the electrons can move into the empty band.

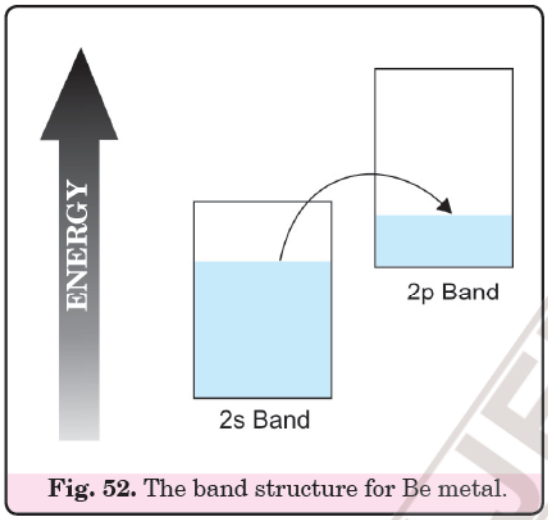

Fig. 52. The band structure for Be metal.

Thus, if the band is partially filled or it overlaps with a higher energy unoccupied band, then electrons can easily flow under an applied electric field and metal shows conductivity. For example, a partially filled band is shown in Fig. 53. (*a*) and overlapping bands are shown in Fig. 53(*b*) found in metals. Therefore, when some electric field is applied electrons can easily move within partially filled band or empty overlapping band and this movement is responsible for electrical conductance of the substance. This type of behaviour is shown by metals.

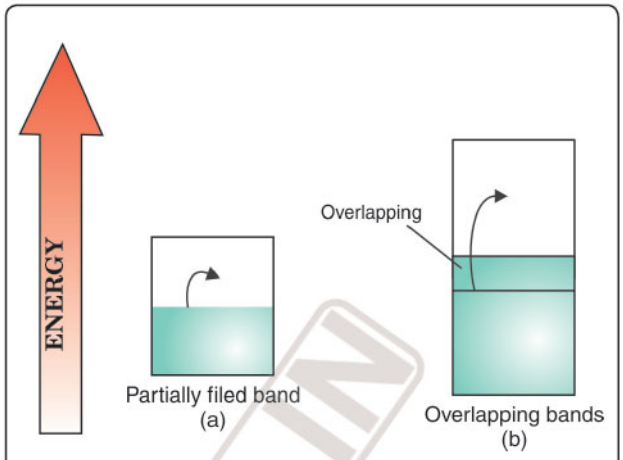

Fig. 53. Partially filled and overlapping bands.

In general, the electrical conductance of solids depends upon the energy gap between the filled valence bands and next higher vacant energy band.

- The *outermost filled energy band is called* **valence band** *and*
- *the next (lowest lying) empty band in which electrons can move is called* **conduction band.**

The spaces between valence band and conduction band represent energies forbidden to electrons and are called **energy gaps** or **forbidden zone.** The valence band and conduction bands for metals, semi-conductors and insulators are shown in Fig. 54.

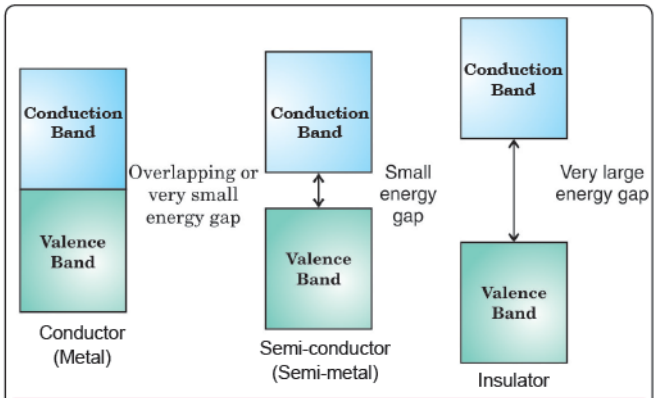

Fig. 54. Valence and conductance bands in metals, semi-conductors and insulators.

(*i*) In **metals**, the *conduction band is close to valence band* and, therefore, the electrons can easily go into the conduction band. Therefore, metals are good **conductors**.

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(*ii*) In **insulators**, *the energy gap between valence band and conduction band is very large.* Therefore, the electrons from valence band cannot jump into the conduction band. Hence, the insulators have extremely low conductivity.

(*iii*) Several solids have properties intermediate between metals and insulators. These are called **semi-metals** or **semiconductors**. They have only small difference in energy between the filled valence band and empty conduction band. Therefore, some electrons may jump to conduction band and hence they show some conductivity. *Electrical conductivity of semi-conductors increases with rise in temperature because more electrons can jump to the conduction band.* Substances like silicon and germanium show this type of behaviour.

Conduction of Electricity in Semiconductors

Germanium and silicon are the most important commercial examples of semiconductors. Atoms of both germanium and silicon have four electrons in the outermost shell. Therefore, each atom is covalently bonded with four neighbouring atoms. There are no free electrons in this structure and therefore for practical purposes, the conductivities of pure germanium and silicon are very low and they behave as insulators. The energy gap between valence band and conduction band for Ge and Si are 68 kJ mol^{-1} and 106 kJ mol^{-1} respectively at room temperature.

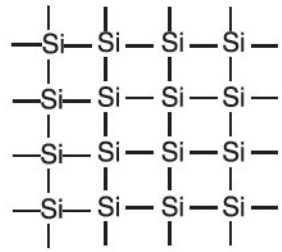
These can behave as semi-conductors in two types :

(*i*) *Intrinsic conduction*

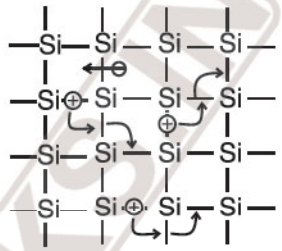
(*ii*) *Extrinsic conduction*

(*i*) Intrinsic conduction

Pure silicon or germanium are poor conductors because they have network or lattice of four strong covalent bonds. [Fig. 55 (*a*)] When a sufficient amount of energy by increasing temperature is supplied to the crystal, some covalent bonds may break due to thermal vibrations and electrons are released. When the crystal is connected to the elecric current, these electrons move leaving behind a positive charge or a 'positive hole' at the site of missing electron. The crystal will now be able to conduct electricity because when electric field is applied, the electrons move in one direction and the 'positive holes' move in the other direction. The electrons move through the interstices of the lattice and the positive holes jump from one bond to another as shown in Fig. 55 (*b*). This is known as **intrinsic semiconductivity of the crystal.** The intrinstic semiconductor contains equal number of current carrying holes and electrons.



(*a*) Network of pure silicon



(*b*) Intrinsic semi-conduction in silicon

Fig. 55. (*a*) Pure silicon (*b*) Silicon showing positive holes and negative electrons.

(*ii*) Extrinsic semi-conduction

The conductivity of the intrinsic semiconductors is too low to be of practical use. Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called **doping**. The conductivity of silicon and germanium increases drastically by doping it with certain other elements.

The impurities are of two types :

(*i*) Electron rich (or donor) impurities and

(*ii*) Electron deficient (or acceptor) impurities.

(*i*) Electron rich (or donor) impurities. The electron rich (or donor) impurities provide electrons in the following way:

Silicon and germanium belong to group 14 of the periodic table and have four valence electrons. In their crystals each atom forms four covalent bonds (as discussed above) with its neighbours (Fig. 55).

Let us consider that some atoms with five valence electrons (of group 15) such as arsenic (As) are added to the silicon crystal. As a result, silicon atoms at some lattice sites are replaced by As atoms with five electrons in their outermost shell. As a Si atom is substituted by an atom of As, four of the electrons in arsenic form covalent bonds with surrounding Si atoms and the fifth electron remains free. Hence, an extra electron, over and above the number required for forming the four covalent bonds, gets introduced in the crystal. This extra electron which is not needed for bonding becomes delocalised and can serve to conduct electricity and therefore, silicon containing traces of arsenic (or arsenic doped silicon) exhibits high electrical

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conductivity. This type of conduction is known as ***n*-type semi-conduction** where '*n*' stands for negative because electrons are responsible for semiconducting behaviour. This is shown in Fig. 56. Doping of a germanium or silicon semiconductor with other group-15 elements such as P, Sb or Bi also give *n*-type semiconductors.

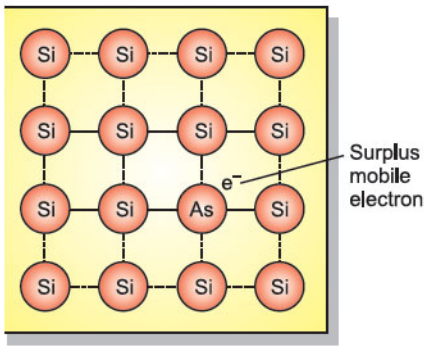

Fig. 56. Arsenic doped silicon semi-conductor.

***(ii)* Electron deficient or Acceptor Impurities.** An electron deficient or Acceptor impurity helps in conduction in the following way :

Suppose some atoms of silicon are doped with acceptor atoms having only three outer shell electrons such as indium (of Group 13). As a result, silicon atoms at some sites are replaced by indium atoms with three electrons in their outermost shell. Each indium atom uses its three electrons to form three bonds in the lattice and some sites normally occupied by electrons will be left empty and gives rise to electron deficiencies. The electron deficient sites are called **electron vacancies** or **electron holes**. An electron from neighbouring atom can jump to fill up this electron hole, but in doing so it would create an electron hole at its original position. As it continues, it would appear as if the electron hole has moved in the direction opposite to that of electron which filled it. When an electric field is applied, the electrons move towards the positively charged plate through electron holes and electron holes move towards the negatively charged plate as if they carry positive charge. This type of semiconductors are called ***p*-type semiconductors** because holes (positive in charge) appear to be responsible for the semiconducting properties. Doping of silicon or germanium with other group-13 elements such as B, Al or Ga also give *p*-type semiconductors. This is shown in Fig. 57.

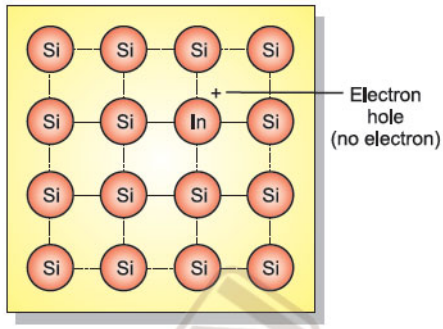

Fig. 57. Indium doped silicon semiconductor.

Thus, doping of germanium or silicon with traces of arsenic (or other group-15 element) gives rise to *n*-type semi-conductor and that with indium (or other group 13 element) gives rise to *p*-type semiconductor. Both *n*-type and *p*-type semiconductors are electrically neutral because each atom of impurity added is neutral in itself containing equal number of protons and electrons.

Applications of *n*-type and *p*-type semiconductors.

n-type and *p*-type of semiconductors are shown in Fig. 58. Various combinations of *n*-type and *p*-type semiconductors are possible which are used to make electronic components. For example,

- A **diode** is a combination of *n*-type and *p*-type semi-conductors and is used as a rectifier.
- Transistors which are *p*-*n*-*p* or *n*-*p*-*n* 'sandwich' semi-conductors are used to detect or amplify radio or audio signals.

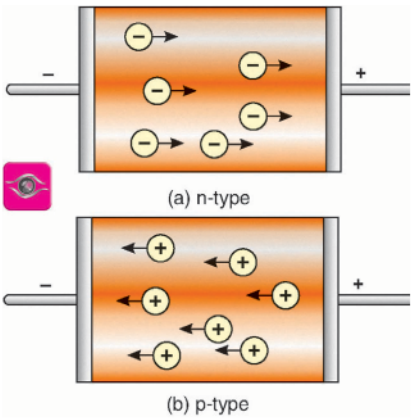

Fig. 58. Conduction in *n*-type and *p*-type of semiconductors.

- A solar cell is a photo diode used for converting radiant energy (of light) into electrical energy.
- Now, a large variety of solid materials have been prepared by combination of elements

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of group-13 and 15 or 12 and 16 which have average valence of 4 as in Ge or Si. Typical examples of group 13–15 compounds are AlP, GaAs or InSb. Gallium arsenide (GaAs) semiconductors have gained much response and have revolutionised the design of semiconductor devices. The examples of group 12–16 compounds are ZnS, CdS, CdSe and HgTe. In these compounds, the bonds are not perfectly covalent and the ionic character depends upon the electronegativity differences between the two elements.

It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, VO, CrO_2 and ReO_3 behave like typical metals. Rhenium oxide, ReO_3 behaves metallic like copper in conductivity and appearance. Certain other oxides like VO, VO_2, VO_3 and TiO_3 show metallic or insulating properties depending upon temperature.

Competition Plus

Superconducting materials are those which offer no resistance to the passage of electricity. For detail, refer **Competition File** (Page 78A).

2. Magnetic Properties of Solids

The microscopic (observable) magnetic properties of materials are due to the magnetic moments associated with individual electron. Each electron in an atom has magnetic moment which originates from two sources :

(i) Orbital motion around the nucleus.

(ii) Spin of electron around its own axis.

A moving electron may be regarded as a small current loop generating a small magnetic field and having a magnetic moment along its axis of rotation as shown in Fig. 59 (*a*). The magnetic moment which originates from electron spin is directed along the spin axis. The spin magnetic moments are generally shown by up and down direction as shown in Fig. 59 (*b*). Thus, each electron in an atom may be regarded as a small magnet having permanent orbital and spin magnetic moments. The fundamental magnetic moment is the **Bohr magneton** μ_B which is equal to 9.27×10^{-24} A m^2. For each electron in an atom, the spin magnetic moment is $\pm \mu_B$ depending upon the two possibilities of the spin. The contribution of the orbital magnetic moment is equal to $m_l \mu_B$ where m_l is the **magnetic quantum number** of the electron.

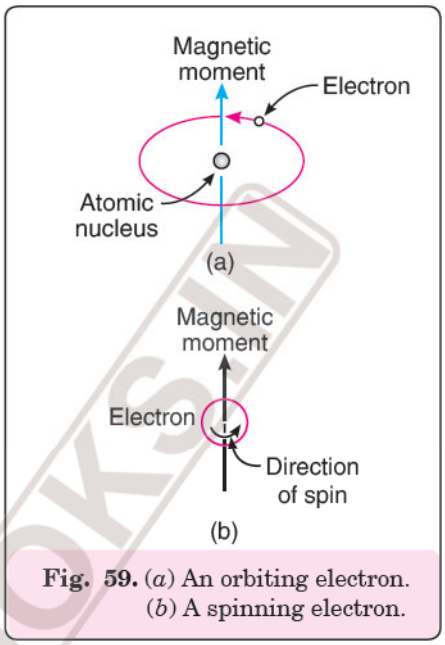

Fig. 59. (*a*) An orbiting electron. (*b*) A spinning electron.

The magnetic properties of solids are also related to their electronic structures. Materials can be divided into the following types depending upon their response to magnetic field :

(*i*) Diamagnetic materials. *The substances which are weakly repelled by the magnetic field* are known as **diamagnetic substances**. For example, NaCl, water, benzene, etc. are diamagnetic substances. The property thus exhibited is called **diamagnetism**. Diamagnetism arises when all the electrons are paired. Pairing of electrons cancels their magnetic moments and they lose their magnetic character.

(*ii*) Paramagnetic materials. *The substances which have permanent magnetic dipoles and are attracted by the magnetic field are known* as **paramagnetic substances**. These consist of atoms, ions or molecules having one or more unpaired electrons. The common examples are Cu^{2+}, Fe^{3+}, Cr^{3+}, O_2, TiO, Ti_2O_3, VO_2, CuO, etc. They lose their magnetism in the absence of magnetic field. Solids like TiO_2 which are expected to be diamagnetic often show paramagnetism due to the presence of slight non-stoichiometry.

(*iii*) Ferromagnetic substances. *The substances which are strongly attracted by the magnetic field and show permanent magnetism even when the magnetic field is removed* are known as

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ferromagnetic substances. Once such a material is magnetised, it remains magnetised permanently. Iron is the most common example. Other examples are cobalt, nickel, gadolinium (Gd), CrO_2, etc. at room temperature. These substances are very important in technology. For example, CrO_2 is the oxide used to make magnetic tapes for use in cassette recorders.

In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called **domains.** Thus, each domain acts as a tiny magnet. In an unmagnetized piece of ferromagnetic substance, the domains are randomly oriented and their magnetic moments get cancelled. When the substance is placed in a magnetic field all the domains get oriented in the direction of magnetic field. Depending upon the alignment of magnetic moments of domains in ferromagnetic substances, these are divided into three types :

(*a*) *When there is spontaneous alignment of magnetic moments of domains in the same direction, we get* **ferromagnetism** [Fig. 60 (*a*)].

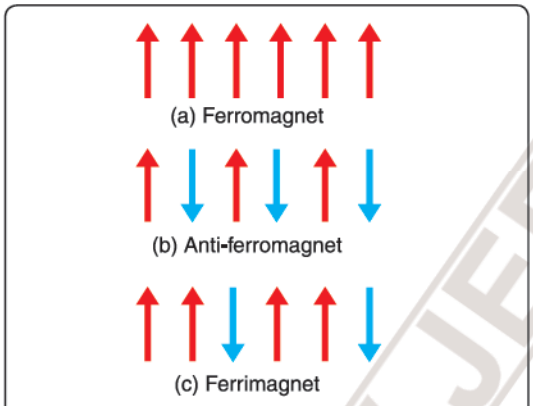

Fig. 60. Alignment of magnetic moments in (*a*) Ferromagnet (*b*) Anti-ferromagnet (*c*) Ferrimagnet.

These have strong magnetic effect. This ordering of domains persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.

(*b*) *If the alignment of magnetic moments of domains is in a compensatory way so as to give zero net magnetic moment because of cancellation of the individual magnetic moments then we get* **anti-ferromagnetism** in the material. The common example is MnO. A pattern of alignment of magnetic domains in anti-ferromagnetic substance is shown in Fig. 60 (*b*).

(*c*) *When the magnetic moments of domains are aligned in parallel and anti-parallel directions in unequal numbers resulting in net magnetic moment, we get* **ferrimagnetism**. This is shown in Fig. 60 (*c*). They are weakly attracted by magnetic field as compared to ferromagnetic substances. For example, Fe_3O_4 (magnetite) and ferrites of formula $M^{2+}Fe_2O_4$; M = Mg, Cu, Zn, etc show ferrimagnetism. These substances also lose ferrimagnetism on heating and become paramagnetic.

It may be noted that all the magnetically ordered solids (ferromagnetic, anti-ferromagnetic and ferrimagnetic) transform to paramagnetic state at a higher temperature due to randomisation of their spins. For example,

(*i*) V_2O_3 transforms from anti-ferromagnetic state to paramagnetic state at 150 K.

(*ii*) Fe_3O_4 becomes paramagnetic from ferrimagnetic at 850 K.

Magnetic properties of some transition metal oxides are shown below (where p = paramagnetic, af = anti-ferromagnetic, fe = ferrimagnetic, f = ferromagnetic and d = diamagnetic)

TiO (p)	VO (p)		MnO (af)	FeO (af)	CoO (p)	NiO (p)	CuO (p)
Ti_2O_3 (p)	V_2O_3 (af)	Cr_2O_3 (af)	Mn_2O_3 (af)	Fe_2O_3 (af)			
TiO_2 (d)	VO_2 (p)	CrO_2 (f)	MnO_2 (af)	Fe_3O_4 (fe)	Co_3O_4 (af)		
	V_2O_5 (d)						

REMEMBER

It may be noted that each ferromagnetic substance has a characteristic temperature above which no ferromagnetism is observed. This is known as **Curie temperature.**

Competition Plus

Solids have dielectric properties.For detail, refer **Competition File** (Page 78A).

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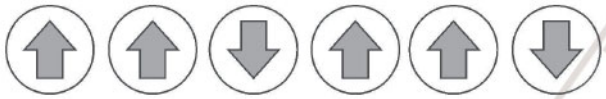
add on

Conceptual Questions 2A

Q.1. Analysis shows that FeO has a non-stoichiometric composition with molecular formula $Fe_{0.95}O$. Give reason. ***(A.I. S.B. 2018)***

Ans. It shows metal deficiency defect. In FeO, some Fe^{2+} ions are replaced by Fe^{3+} ions. Three Fe^{2+} ions are replaced by two Fe^{3+} ions to maintain electrical neutrality.

Q.2. Following is the schematic alignment of magnetic moments:



Identify the type of magnetism. What happens when these substances are heated ? ***(CBSE Sample Paper 2017-18)***

Ans. Ferrimagnetism. These substances lose ferrimagnetism on heating and become paramagnetic.

Q.3. Name any one solid in which both Frenkel and Schottky defects occur.

Ans. Silver bromide, AgBr has both Frenkel and Schottky defects.

Q.4. What is the effect of temperature on the conductivity of metals and semi-metals ?

Ans. In general, with increase in temperature, the conductivity of metals decreases and that of semi-metals increases.

Q.5. What is photovoltaic cell ?

Ans. The process in which electricity is produced by shining sunlight on certain substances. Amorphous silicon acts as a typical photovoltaic cell.

Q.6. Why is Frenkel defect not found in pure alkali metal halides ?

Ans. Frenkel defect is not found in alkali metal halides because the ions cannot get into the interstitial sites due to their larger size.

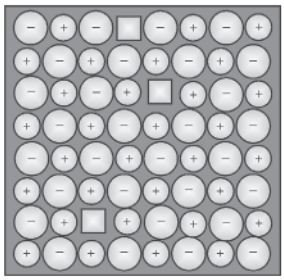
Q.7. What is the effect of presence of Schottky defects on the density of the crystal ?

Ans. The overall density of a crystalline substance decreases due to Schottky defects.

Q.8. What is the difference in the semi-conductors obtained by doping silicon with As or with Ga?

Ans. Semi-conductor produced by doping silicon with As is *n-type semiconductor* in which flow of current is due to electrons while silicon doped with Ga is *p*-type *semiconductor* in which flow of current is due to positive holes.

Q.9. Identify the type of defect shows in the following figure: What type of substances show this defect ? ***(CBSE Sample Paper 2017-18)***



Ans. Schottky defect.
This type of defect is shown by ionic compounds in which
(*i*) the ions have high coordination number and
(*ii*) ions (cations and anions) are of almost similar sizes.

Q.10. Classify each of the following as being either a *p*-type or *n*-type semiconductor :

(*i*) Ge doped with In.

(*ii*) Si doped with B. ***(CBSE Sample Paper 2011)***

Ans. (*i*) Ge belongs to group 14 and In belongs to group 13.

Therefore, an electron deficient hole is created and it is a ***p*-type semiconductor.**

(*ii*) B belongs to group 13 and Si belongs to group 14. Therefore, an electron deficient hole is created and it is a ***p*-type semiconductor.**

Q.11. Name a salt which is added to AgCl so as to produce cation vacancies. ***(A.I.S.B. 2003, D.S.B. 2004)***

Ans. $CdCl_2$.

CONCEPTUAL QA

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Q.12. Which point defect lowers the density of a crystal ? ***(A.I.S.B. 2004)***

Ans. Schottky defect.

Q.13. How does the electrical conductivity of semi-conductors vary with temperature ? ***(Pb.S.B. 2006)***

Ans. The electrical conductivity of semi-conductors increases with increase in temperature.

Q.14. Name the non-stoichiometric point defect responsible for colour in alkali metal halides. ***(A.I.S.B. 2006)***

Ans. Metal excess non-stoichiometric point defects.

Q.15. $CaCl_2$ will introduce Schottky defect when added to AgCl crystal. Explain. ***(Pb.S.B. 2003)***

Ans. $CaCl_2$ on adding to AgCl introduces impurity defect. The addition of one Ca^{2+} ion will replace two Ag^+ ions to maintain electrical conductivity. One of the position of Ag^+ will be occupied by Ca^{2+} ion and other will be left as a hole. Thus, a hole is created similar to Schottky defect.

Q.16. Why does ZnO appear golden yellow at high temperature? Explain. ***(Meghalaya S.B. 2013, Kerala S.B. 2018))***

Ans. When ZnO is heated it loses oxygen as :

$$ZnO \xrightarrow{\text{Heat}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

The Zn^{2+} ions are entrapped in the interstitial sites and electrons are entrapped in the neighbouring interstitial sites to maintain electrical neutrality. This results in metal excess defect. Due to the presence of electrons in the interstitial void, the colour is yellow.

Q.17. The electrical conductivity of metals decreases with rise in temperature while that of a semiconductor increases. Explain. ***(H.P.S.B. 2003)***

Ans. In case of metals, with increase in temperature, the kernels start vibrating and therefore, they offer resistance to the flow of electrons. Hence, conductivity of metals decreases with rise in temperature. On the other hand, in case of semi-conductors, the conducitivity is due to the presence of impurities and defects. As the number of defects (such as holes) increases with rise in temperature, the conductivity increases.

Q.18. Why does zinc oxide exhibit enhanced electrical conductivity on heating ? ***(D.S.B. 2005 C)***

Ans. On heating, zinc oxide loses oxygen as :

$$ZnO \xrightarrow{\text{Heat}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

The zinc ions thus formed are entrapped into the interstitial sites while the electrons are entrapped in the neighbouring interstitial sites. The entrapped electrons enhance the electrical conductivity of ZnO.

Q.19. Give reason :

(a) Why is Frenkel defect found in AgCl ?

(b) What is the difference between phosphorus doped and gallium doped silicon semi-conductors ? ***(CBSE Sample Paper 2011)***

Ans. (a) Due to small size of Ag^+ ion, it can fit into interstitial sites.

(b) Phosphorus doped silicon are *n*-type semiconductors while gallium doped silicon are *p*-type semiconductors.

Q.20. Why does LiCl acquire pink colour when heated in Li vapours ? ***(CBSE Sample Paper 2011)***

Ans. On heating LiCl in Li vapours, the excess of Li atoms deposit on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Li atoms to form LiCl. The electrons produced by ionisation of Li atoms diffuse into the crystal and get trapped at anion vacancies called F-centres. These absorb energy from visible light and radiate pink colour.

CONCEPTUAL QA

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Solution File

Hints & Solutions for Practice Problems

❑ **1.** As Y atoms are at the corners of the cube and contribution of each = 1/8, therefore, no. of Y atoms/unit cell = $8 \times \frac{1}{8} = 1$. There can be only one X atom at the body centre.
Hence, formula = **XY.**

❑ **2.** There are only 8 corners so, no. of atoms per unit cell = $8 \times \frac{1}{8} = 1$

❑ **3.** No. of A atoms at the corners = 8
No. of A atoms missing from corners = 2
No. of A atoms present = 8 – 2 = 6

No. of A atoms per unit cell = $\frac{6}{8} = 3/4$

No. of B atoms per unit cell = $6 \times \frac{1}{2} = 3$

$\therefore$ Formula = $A_{3/4}B_3$ = **AB_4.**

❑ **4.** There are 8 Y atoms at the corners and contribution of each is 1/8.

$\therefore$ No. of Y atoms per unit cell = $8 \times \frac{1}{8} = 1$

There can be only two X atoms at alternate faces and contribution of each of them is 1/2.

$\therefore$ No. of X atoms per unit cell = $2 \times \frac{1}{2} = 1$

Hence, formula is **XY.**

❑ **5.** 1 mole of gold = 197 g = 6.02×10^{23} atoms
No. of atoms in 2×10^{-3} g of gold

$$= \frac{6.02 \times 10^{23}}{197} \times 2 \times 10^{-3}$$

$$= 6.11 \times 10^{18}$$

Since face centred cubic unit cell contains 4 atoms, therefore, number of unit cells present

$$= \frac{6.11 \times 10^{18}}{4} = \mathbf{1.528 \times 10^{18}} \text{ unit cells}$$

❑ **6.** Distance between nearest neighbour.

$$d = \frac{a}{\sqrt{2}} = \frac{620}{\sqrt{2}} = 438.5 \text{ pm}$$

$$r = \frac{d}{2} = \mathbf{219.25 \text{ pm}}$$

❑ **7.** For *bcc* crystal, $r = \frac{\sqrt{3}}{4}a$

$$= \frac{1.732 \times 352}{4} = \mathbf{152.416 \text{ pm}}$$

❑ **8.** For *fcc* unit cell, radius

$$r = \frac{a}{2\sqrt{2}}$$

$$r = \frac{4.086 \times 10^{-10} \text{ m}}{2 \times 1.414} = \mathbf{1.44 \times 10^{-10} \text{ m.}}$$

❑ **9.** No. of W atoms = $8 \times 1/8 = 1$

No. of O atoms = $12 \times \frac{1}{4} = 3$

No. of Na atoms= 1

Formula = **$NaWO_3$**

❑ **10.** We assume that the closest Cs^+ to Cl^- ion distance is the sum of ionic radii of Cs^+ and Cl^- ions.
Nearest neighbour distance = 1.69 + 1.81 = 3.50Å
This distance is one half of the body diagonal of the cube

Body diagonal = $\sqrt{3}a$

$$\therefore \quad \frac{\sqrt{3}a}{2} = 3.50$$

or $$a = \frac{3.50 \times 2}{\sqrt{3}} = \mathbf{4.04Å.}$$

❑ **11.** 1 mol of tungsten = 184g = 6.022×10^{23} atoms

No. of atoms in 1.5g of tungsten = $\frac{6.022 \times 10^{23}}{184} \times 1.5$

$$= 4.909 \times 10^{21}$$

A bcc unit cell contains 2 atoms per unit cell.

$\therefore$ No. of unit cells = $\frac{4.909 \times 10^{21}}{2} = \mathbf{2.45 \times 10^{21}}$

❑ **12.** 1 mol of sodium = 23 g = 6.022×10^{23} atoms
No. of atoms present in 9.2 g of sodium

$$= \frac{6.022 \times 10^{23}}{23} \times 9.2 = 2.4088 \times 10^{23}$$

A *bcc* unit cell contains 2 atoms,

$\therefore$ No. of unit cells present = $\frac{2.4088 \times 10^{23}}{2}$

$$= \mathbf{1.2044 \times 10^{23}}$$

❑ **13.** For face centred unit cell, radius of atom

$$r = \frac{a}{2\sqrt{2}}$$

or $$a = 2\sqrt{2}.r$$

$$r = 0.144 \text{ nm}$$

$\therefore$ $$a = 2 \times 1.414 \times 0.144$$

$$= \mathbf{0.407 \text{ nm.}}$$

❑ **14.** No. of atoms of A at corners = 7 (because one A is missing).
Contribution of atoms A in a unit cell = $7 \times \frac{1}{8} = \frac{7}{8}$

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No. of atoms of B at face centres = 6

$\therefore$ Contribution of atoms B in a unit cell = $6 \times \frac{1}{2} = 3$

A : B = $\frac{7}{8} : 3$ or 7 : 24

$\therefore$ Simplest formula = $\mathbf{A_7B_{24}}$

❑ **15.** $\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{1.69\text{Å}}{1.81\text{Å}} = 0.934$

Since the radius ratio lies between 0.732 to 1, the coordination number of Cs^+ is 8 and the geometry of CsCl is cubic.

❑ **16.** $r_{B^-} = \frac{r_{A^+}}{0.414}$ to $\frac{r_{A^+}}{0.732}$

$= \mathbf{241.6}$ to $\mathbf{136.6}$ **pm**

❑ **17.** For a cation to fit into a tetrahedral hole

$$\frac{r_+}{r_-} < 0.414$$

or $r_+ < 0.414 \times r_-$

$< 0.414 \times 0.182$ nm

$\therefore$ $r_+ < 7.53 \times 10^{-2}$ nm

❑ **18.** For each X atom, there are one octahedral and two tetrahedral sites.

No. of Y atoms in octahedral sites = 1 per X atom

Since alternative (*i.e.,* half) tetrahedral sites are occupied,

No. of Y atoms in tetrahedral sites = 1 per X atom

Total Y atoms = 2 per X atom

$\therefore$ Formula = $\mathbf{XY_2}$.

❑ **19.** Suppose number of atoms of Y in *ccp* = N

No. of octahedral voids = N

No. of atoms of X = N

Formula : **XY**

❑ **20.** Since N forms *ccp* arrangement, it will have 4 atoms in a unit cell.

Number of N atoms in unit cell = 4

For each atom, there are two tetrahedral voids so that there are 8 tetrahedral voids per unit cell.

No. of M atoms = $\frac{1}{3} \times 8 = \frac{8}{3}$

Formula = $M_{8/3}N_4$

or $= \mathbf{M_2N_3}$.

❑ **21.** Suppose the number of anions Y = N

No. of octahedral voids = N

No. of tetrahedral voids = 2 N

Since octahedral and tetrahedral voids are equally occupied by cations X and all the octahedral voids are occupied (as given) then N cations X are present in octahedral voids and N cations X are present in tetrahedral voids. Therefore,

No. of cations present = N + N = 2N

Ratio of cations X and anions Y = 2N : N

or 2 : 1

Thus, the formula of the compound will be $\mathbf{X_2Y}$.

❑ **22.** Suppose the number of oxide ions = N

No. of octahedral voids = N

No. of tetrahedral voids = 2 N

No. of cations P present = $\frac{1}{6} \times 2N = \frac{1}{3}N$

No. of cations Q present = $\frac{1}{3} \times N = \frac{N}{3}$

Ratio P : Q : O^{2-}

$\frac{N}{3} : \frac{N}{3} : N$ or 1 : 1 : 3

Formula of compound = $\mathbf{PQO_3}$.

❑ **23.** In *hcp* arrangement, there is one octahedral void corresponding to each atom in the close packing.

Since $\frac{2}{3}$ of the octahedral voids are occupied by aluminium ions, therefore, for each oxide ion there will be $\frac{2}{3}$ aluminium ions.

Therefore, ratio between aluminium ion and oxide ion is :

$\frac{2}{3} : 1$ or 2 : 3

Formula of corrundum = $\mathbf{Al_2O_3}$.

❑ **24.** $d = \frac{Z \times M}{a^3 \times N_A}$

$= \frac{4 \times 40}{(400 \times 10^{-10})^3 \times 6.022 \times 10^{23}}$

$= \mathbf{4.15\ g\ cm^{-3}}$

40 g of element = 6.022×10^{23} atoms

4 g of element = $\frac{6.022 \times 10^{23}}{40} \times 4$

$= 6.022 \times 10^{22}$ atoms

For fcc, Z = 4

1 unit cell = 4 atoms

No. of unit cells in 4g = $\frac{6.022 \times 10^{22}}{4}$

$= \mathbf{1.505 \times 10^{22}}$

❑ **25.** Edge length = 400 pm = 400×10^{-10} cm

Volume of unit cell = $(400 \times 10^{-10})^3 = 64 \times 10^{-24}$ cm^3

Volume of 280 g of element = $\frac{280\ g}{7\ g\ cm^{-3}} = 40\ cm^3$

Number of unit cells in this volume

$= \frac{40}{64 \times 10^{-24}} = 6.25 \times 10^{23}$

For *fcc*, number of atoms per unit cell = 4

$\therefore$ No. of atoms in 280 g of element = $6.25 \times 10^{23} \times 4$

$= \mathbf{2.5 \times 10^{24}}$ **atoms**

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❑ **26.** Volume of 50 g of element $= \frac{50}{19.35}$

$= 2.59\ cm^3$

Volume of unit cell $= (3.16 \times 10^{-8})^3$

$= 31.6 \times 10^{-24}\ cm^3$

No. of unit cells in this volume $= \frac{2.59}{31.6 \times 10^{-24}}$

$= 8.2 \times 10^{22}$

Since *bcc* arrangement has 2 atoms per unit cell,

Total no. of atoms $= 2 \times 8.2 \times 10^{22} =$ **1.64×10^{23}.**

❑ **27.** Volume of unit cell of CsCl $= (4.121 \times 10^{-8})^3$

$= 69.99 \times 10^{-24}\ cm^3$

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$Z = 1$ (for *bcc*)

Formula mass $= 132.9 + 35.5 = 168.4$

The unit cell contains one Cs^+ ion and one Cl^- ion *i.e.,* one formula unit of CsCl.

$$\text{Density (CsCl)} = \frac{1 \times 168.4}{(412.1 \times 10^{-10})^3 \times (6.022 \times 10^{23})}$$

$=$ **$3.995\ g\ cm^{-3}$**

For Al, $Z = 4$

$$\text{Density (Al)} = \frac{4 \times 26.9}{(405 \times 10^{-10})^3 \times (6.022 \times 10^{23})}$$

$=$ **$2.690\ g\ cm^{-3}$.**

CsCl has larger density.

❑ **28.** $$\rho = \frac{Z \times M}{a^3 \times N_A}$$

$a = 409\ pm = 409 \times 10^{-10}\ cm$

$$10.5 = \frac{Z \times 108}{(409 \times 10^{-10})^3 \times (6.022 \times 10^{23})}$$

$$\therefore Z = \frac{10.5 \times (409 \times 10^{-10})^3 \times (6.022 \times 10^{23})}{108} = 4.0$$

$\therefore$ ***fcc* type structure**

❑ **29.** Density, $$\rho = \frac{Z \times M}{a^3 \times N_A}$$

$a = 286.65 \times 10^{-10}$ cm, $Z = 2$ (for *bcc*)

$M = 55.845$ u, $\rho = 7.874\ g\ cm^{-3}$

$$7.874 = \frac{2 \times 55.845}{(286.65 \times 10^{-10})^3 \times N_A}$$

$$\text{or } N_A = \frac{2 \times 55.845}{(286.65 \times 10^{-10})^3 \times 7.874} =$$ **6.022×10^{23}**

❑ **30.** Density, $$\rho = \frac{Z \times M}{a^3 \times N_A}$$

For *fcc* unit cell, $r = \frac{a}{2\sqrt{2}}$

$a = 2\sqrt{2}r = 2 \times 1.414 \times 0.144$

$= 0.407\ nm = 0.407 \times 10^{-7}\ cm$

$$\rho = \frac{4 \times (197\ g\ mol^{-1})}{(0.407 \times 10^{-7}\ cm)^3 \times (6.022 \times 10^{23}\ mol^{-1})}$$

$=$ **$19.41\ g\ cm^{-3}$**

❑ **31.** $$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$Z = 4$ (for *fcc*)

$$6.23 = \frac{4 \times 60}{a^3 \times 6.022 \times 10^{23}}$$

$$a^3 = \frac{4 \times 60}{6.23 \times 6.022 \times 10^{23}}$$

$= 64 \times 10^{-24}$

$a = 4 \times 10^{-8}$ cm

$=$ **4×10^{-10} m $= 400$ pm.**

❑ **32.** Density, $$\rho = \frac{Z \times M}{a^3 \times N_A}$$

$\rho = 10\ g\ cm^{-3}$, $M = 81\ g\ mol^{-1}$

$a = 3 \times 10^{-8}$ cm, $N_A = 6.022 \times 10^{23}$

$$\therefore \quad 10 = \frac{Z \times 81}{(3 \times 10^{-8})^3 \times 6.022 \times 10^{23}}$$

$$\text{or} \quad Z = \frac{10 \times (3 \times 10^{-8})^3 \times 6.022 \times 10^{23}}{81} = 2.0$$

$\therefore$ Nature of cubic unit cell is ***bcc***.

❑ **33.** $$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$M = 207 + 32 = 239$

$$= \frac{4 \times 239}{(500 \times 10^{-10})^3 \times (6.022 \times 10^{23})}$$

$=$ **$12.70\ g\ cm^{-3}$**

❑ **34.** Edge of unit cell $= 2 \times 2.814 \times 10^{-8}$ cm

$= 5.628 \times 10^{-8}$ cm

$Z = 4$

If N_A is Avogadro number,

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$M = 202 + 37 = 239$

$$2.167 = \frac{4 \times 58.5}{(5.628 \times 10^{-8})^3 \times N_A}$$

$$N_A = \frac{4 \times 58.5}{(5.628 \times 10^{-8})^3 \times 2.167}$$

$=$ **6.06×10^{23}**

❑ **35.** $$\text{Density} = \frac{4 \times 63.5}{(3.61 \times 10^{-8})^3 \times (6.022 \times 10^{23})}$$

$=$ **$8.96\ g\ cm^{-3}$**

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❑ **36.** Molecular mass of CsBr = 133 + 80 = 213

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$$Z = 1$$

$$4.24 = \frac{1 \times 213}{a^3 \times 6.022 \times 10^{23}}$$

$$\therefore \quad a^3 = \frac{1 \times 213}{6.022 \times 10^{23} \times 4.24}$$

$$= 8.34 \times 10^{-23}$$

$$\therefore \quad a = 4.369 \times 10^{-8} \text{ cm} = \mathbf{436.9\ pm}$$

❑ **37.** $$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$$10.5 = \frac{Z \times 108}{(409 \times 10^{-10})^3 \times 6.022 \times 10^{23}}$$

$$Z = \frac{10.5 \times (409 \times 10^{-10})^3 \times 6.022 \times 10^{23}}{108}$$

$$= \mathbf{4.0}$$

$\therefore$ ***fcc*** type structure.

❑ **38.** $$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$$2.165 = \frac{4 \times 58.5}{a^3 \times 6.022 \times 10^{23}}$$

$$a^3 = \frac{4 \times 58.5}{2.165 \times 6.022 \times 10^{23}}$$

$$a^3 = 179.48 \times 10^{-24} \text{ cm}^3$$

or $$a = 5.64 \times 10^{-8} \text{ cm}$$

In NaCl structure, $a = 2\,(r_{Na^+} + r_{Cl^-})$

$\therefore$ Distance between Na^+ and Cl^- ion,

$$r_{Na^+} + r_{Cl^-} = \frac{a}{2} = 2.82 \times 10^{-8} \text{ cm} = \mathbf{282\ pm}$$

❑ **39.** In a *bcc* lattice,

body diagonal $= \sqrt{3}a$

Now, $$2\,(r_{A^+} + r_{B^-}) = \sqrt{3}a$$

$$r_{A^+} + r_{B^-} = \frac{\sqrt{3}}{2} \times a = \frac{1.732 \times 380}{2} \text{ pm} = \mathbf{329.1\ pm}$$

$$r_{A^+} = 329.1 - r_{B^-} = \mathbf{154.1\ pm}$$

❑ **40.** Formula unit mass of TlCl = 208.37 + 35.5 = 243.87

$$Z = ?$$

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$$7.00 = \frac{Z \times 243.87}{(3.85 \times 10^{-8})^3 \times (6.022 \times 10^{23})}$$

or $$Z = \frac{7.00 \times (3.85 \times 10^{-8})^3 \times (6.022 \times 10^{23})}{243.87}$$

$$= 0.99 \quad \text{or} \quad 1$$

$\therefore$ A unit cell of TlCl contains one formula unit of TlCl.

$\therefore$ It is a simple cubic arrangement.

❑ **41.** $$\text{Density} = 4.0 \text{ g cm}^{-3}$$

$$Z = 1 \text{ (for cubic lattice)}$$

$$4.00 = \frac{1 \times 168.5}{a^3 \times 6.022 \times 10^{23}}$$

or $$a^3 = \frac{168.5}{4.00 \times 6.022 \times 10^{23}}$$

$$= 69.9 \times 10^{-24} \text{ cm}^3$$

$$\therefore \quad a = 4.12 \times 10^{-8} \text{ cm} = \mathbf{412\ pm}$$

❑ **42.** For *fcc*, $Z = 4$

$$a = 408.6 \text{ pm} = 408.6 \times 10^{-10} \text{ cm}$$

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$$= \frac{4 \times (107.9)}{(408.6 \times 10^{-10} \text{ cm})^3 \times 6.022 \times 10^{23}}$$

$$= \mathbf{10.506\ g\ cm^{-3}}$$

❑ **43.** If N_A is Avogadro number,

$$Z = 4 \text{ (for } fcc\text{)}$$

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

Edge of unit cell $= 2 \times 269 = 538$ pm

$$= 538 \times 10^{-10} \text{ cm}$$

$$\therefore \quad 2.48 = \frac{4 \times 58}{(538 \times 10^{-10})^3 \times N_A}$$

$$N_A = \frac{4 \times 58}{(538 \times 10^{-10})^3 \times 2.48}$$

$$= \mathbf{6.007 \times 10^{23}}$$

❑ **44.** If M is the molar mass of copper,

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$$Z = 4 \text{ (for } fcc\text{)}$$

Cell edge, $a = 3.61 \times 10^{-8}$ cm, $N_A = 6.022 \times 10^{23}$

$$8.92 = \frac{4 \times M}{(3.61 \times 10^{-8})^3 \times 6.022 \times 10^{23}}$$

or $$M = \frac{8.92 \times 6.022 \times 10^{23} \times (3.61 \times 10^{-8})^3}{4} = \mathbf{63.2\ g\ mol^{-1}}.$$

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❑ **45.** If N_A is Avogadro number

Edge of unit cell = 288.4 pm = 288.4×10^{-10} cm

$Z = 2$ for *bcc*

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$$\therefore \quad 7.20 = \frac{2 \times 52}{(288.4 \times 10^{-10})^3 \times N_A}$$

$$\text{or} \quad N_A = \frac{2 \times 52}{7.20 \times (288.4 \times 10^{-10})^3}$$

$$= \mathbf{6.02 \times 10^{23}}$$

❑ **46.** $$\rho = \frac{Z \times M}{a^3 \times N_A}$$

$a = 300$ pm $= 300 \times 10^{-12}$ m $= 3 \times 10^{-8}$ cm

$M = 93$ g mol^{-1}, $\rho = 11.5$ g cm^{-3}

$$\therefore \quad 11.5 \text{ g cm}^{-3} = \frac{Z \times 93 \text{ g mol}^{-1}}{(3 \times 10^{-8} \text{cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$\text{or } Z = \frac{(11.5 \text{ g cm}^{-3}) \times (3 \times 10^{-8} \text{cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}{(93 \text{ g mol}^{-1})}$$

$$= 2.01$$

$\therefore$ It is ***bcc*** type

❑ **47.** $Fe_{0.93}O_{1.0}$ is non-stoichiometric and is a mixture of Fe^{2+} and Fe^{3+} ions. Let x atoms of Fe^{3+} ions are present in the compound. This means that x Fe^{3+} ions have been replaced by Fe^{2+} ions.

No. of Fe^{2+} ions $= 0.93 - x$

For electrical neutrality, positive charge on the compound = Negative charge on the compound

$$2(0.93 - x) + 3x = 2$$

$$1.86 + x = 2$$

$$\text{or} \quad x = 0.14$$

$\therefore$ Fraction of $Fe^{3+} = 0.14$, $Fe^{2+} = 0.93 - 0.14 = 0.79$

Thus, the given formula may be represented as

$$Fe^{2+}_{0.79}\ Fe^{3+}_{0.14}\ O^{2-}_{1.0}$$

Total molar mass $= 0.93 \times 56 + 1 \times 16 = 68.08$g

$$\%\text{ of iron present as Fe(III)} = \frac{0.14 \times 56}{68.08} \times 100 = \mathbf{11.5\%}$$

❑ **48.** Let M^{2+} ions in the crystal be x so that M^{3+} ions in the crystal will be $0.96 - x$. Total charge on the compound must be zero, so that

$$+2 \times x + 3\,(0.96 - x) - 2 = 0$$

$$2x - 2.88 - 3x - 2 = 0$$

$$\text{or} \quad x = 0.88$$

$$\therefore \quad \%\text{ of } M^{2+} = \frac{0.88}{0.96} \times 100 = \mathbf{91.67}$$

$$\%\text{ of } M^{3+} = 100 - 91.67 = \mathbf{8.33.}$$

Chapter Summary

Key Terms

- **Isotropic substances.** The substances which show same physical properties (electrical conductivity, thermal conductivity, refractive index etc.) in all directions are called **isotropic substances**.
- **Anisotropic substances.** The substances which show different physical properties (electrical conductivity, thermal conductivity, refractive index, etc.) in different directions are called **anisotropic substances**.
- **Crystal lattice or space lattice.** It is the regular arrangement of the constituent particles (atoms, ions or molecules) of a crystalline solid in three dimensional space.
- **Unit cell.** It is the the smallest three dimensional repeating portion of a space lattice which when repeated over and again in different directions produces the complete crystal lattice.
- **Close packing.** The arrangement in which maximum available space is occupied leaving minimum available space.
- **Interstitial voids or sites.** The holes or voids in the crystal lattice are called **interstitial voids** or **sites**.
- **Coordination number.** It is the number of nearest (or closest) neighbours of any constituent particle in the crystal lattice.
- **Radius ratio.** The ratio of the radius of the cation to the radius of the anion (*i.e.* r_+/r_-) is called **radius ratio**.
- **Disorder or defect.** Any deviation from completely ordered arrangement of constituent particles in a crystal is called disorder or defect.
- **Schottky defect.** The defect in ionic solids in which equal number of cations and anions are missing from their normal sites.
- **Frenkel defect.** The defect in ionic solids in which some cations are missing from normal lattice sites and occupy interstitial sites.

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QUICK CHAPTER ROUND UP

SOLIDS

Crystalline Solids
- Constituent particles have definite geometric arrangement
- long range order
- ➢ NaCl, Cu, Fe, S

Amorphous Solids
- Constituent particles do not have regular arrangement
- short range order
- ➢ glass, rubber, plastics

- Crystalline solids are **anisotropic** (different properties in different directions)
- Amorphous solids are **isotropic** (same properties in all directions)

MOLECULAR
- **Non polar**: Dispersion forces ▸ Ar, I_2, H_2, solid CO_2
- **Polar**: Dipole-dipole forces ▸ HCl, SO_2
- **Hydrogen bonded**: Hydrogen bonding ▸ Ice (H_2O)

IONIC
- Constituents: +ve and –ve ions
- Strong electrostatic forces ▸ NaCl, MgO, CaF_2

METALLIC
- +ve ions in a sea of electrons
- Metallic bonding ▸ Cu, Ag, Fe, Mg

COVALENT OR NETWORK
- Atoms
- Covalent bonds ▸ SiC, quartz, (SiO_2) diamond, graphite, AlN

CRYSTAL SYSTEMS

7 crystal systems ← CRYSTAL SYSTEMS → 14 Bravais lattices

Cubic	Orthorhombic	Tetragonal	Monoclinic	Triclinic	Hexagonal	Rhombohedral
$a = b = c$	$a \neq b \neq c$	$a = b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$	$a = b \neq c$	$a = b = c$
$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = \gamma = 90°$	$\alpha = \gamma = 90°$, $\beta \neq 90°$	$\alpha \neq \beta \neq \gamma \neq 90°$	$\alpha = \beta = 90°$, $\gamma = 120°$	$\alpha = \beta = \gamma \neq 90°$
P, F, B	P, F, B, E	P, B	P, E	P	P	P
(3)	(4)	(2)	(2)	(1)	(1)	(1)

No. of atoms per cubic unit cell
Simple = 1
Body centred = 2
Face centred = 4
End centred = 2

No. of atoms in hcp = 6

Relationship between nearest distance (d) and radius of atom (r)

Simple cubic	$d = a$	$r = a/2$
Face centred cubic	$d = \frac{a}{\sqrt{2}}$	$r = \frac{a}{2\sqrt{2}}$
Body centred cubic	$d = \frac{\sqrt{3}}{2}a$	$r = \frac{\sqrt{3}}{4}a$

No. of tetrahedral sites = 2 per atom
No. of octahedral sites = 1 per atom

CLOSE PACKING

Cubic close or face centred cubic
- ABCABCA .....

Hexagonal close packing
- ABABA .....

PACKING EFFICIENCY

Percentage of total space filled by particles

ccp	*hcp*	*bcc*	simple cubic
74%	74%	68%	52.4%

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The limiting radius ratio (r_c / r_a) and the coordination numbers in different crystals

r_c / r_a	Coordination No.	Arrangement
0.155 – 0.225	3	Planar triangular (*e.g.*, B_2O_3)
0.225 – 0.414	4	Tetrahedral (*e.g.*, ZnS)
0.414 – 0.732	6	Octahedral (*e.g.*, NaCl)
0.732 – 1	8	Body centred cubic (*e.g.*, CsCl)

Mass of atoms of unit cell = No. of atoms in unit cell (Z) × Mass of atom

$$\text{Mass of atom} = \frac{\text{Molar mass (M)}}{\text{Avogadro number } (N_A)}$$

$$\text{Density of unit cell} = \frac{Z \times M}{a^3 \times N_A}$$

Z for
fcc = 4
bcc = 2
simple cubic = 1

DEFECTS IN CRYSTALS

Stoichiometric

Frenkel defect
- cations missing from normal sites and occupy interstitial sites
- does not cause change in density
  - AgCl, AgBr, AgI, ZnS

Schottky defect
- equal number of cations and anions missing from normal sites
- density decreases
  - NaCl, KCl, CsBr, AgBr

Non-stoichiometric

Metal excess type
- anion vacancies or interstitial cations
- *n*-type semiconductors

Metal deficient type
- cations vacancies or interstitial anions
- *p*-type semiconductors

In AgBr, both Frenkel and Schottky defects occur

SOLIDS ON THE BASIS OF ELECTRICAL PROPERTIES

Conductors
Electrical conductivity:
10^4 to 10^7 $ohm^{-1}m^{-1}$

Semiconductors
Electrical conductivity:
10^{-6} to 10^4 $ohm^{-1}\ m^{-1}$

Insulators
Electrical conductivity:
10^{-20} to 10^{-10} $ohm^{-1}\ m^{-1}$

- ***n*-type semiconductors:** Group 14 elements doped with group 15 elements, free electrons increase conductivity.
- ***p*-type semiconductors:** Group 14 elements doped with group 13 elements, presence of holes increase conductivity.

MAGNETIC PROPERTIES OF SOLID

Paramagnetic
permanent magnetic dipoles and attracted by magnetic field
- O_2, Cu^{2+}, Fe^{3+}, TiO Cuo, TiO_3, VO

Diamagnetic
weakly repelled by magnetic field
- benzene, NaCl, TiO_2, V_2O_3

Ferromagnetic
remain permanently, magnetised even in the absence of magnetic field
- Fe, CO, Ni, CrO_2

Anti-ferromagnetic
zero magnetic moment due to equal number of magnetic moments in opposite directions.
- MnO, FeO, Cr_2O_3

Ferrimagnetic
magnetic moments are aligned in parallel and anti-parallel directions in unequal numbers giving net small magnetic moment .
- $MgFe_2O_4$

- **Curie temperature:** Temperature above which ferromagnetism is not observed.
- **Bragg's equation:** $n\lambda = 2\ d\ \sin\theta$

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NCERT FILE Solved

NCERT In-text Question

Q.1. Why are solids rigid ?

Ans. In solids, the particles are closely packed and the empty spaces between the particles are very small. Therefore, solids are incompressible and they maintain their own shape when subjected to outside force. Hence, solids are rigid.

Q.2. Why do solids have a definite volume ?

Ans. The intermolecular forces between the particles in the solid state are very strong. Therefore, they are strongly held at fixed positions and particles cannot separate from one another. Hence, solids have a definite volume.

Q.3. Classify the following as amorphous or crystalline solids :

Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinylchloride, fibre glass, copper.

Ans. *Refer Solved Example 1* (*Page 7*).

Q.4. Why is glass considered a super cooled liquid ?

Ans. Glass is an amorphous solid. Like liquids, it has a tendency to flow, though very slowly. Moreover, glass is obtained when molten silicates are allowed to cool rapidly. Therefore, glass is considered as a super cooled liquid.

Q.5. Refractive index of a solid is observed to have the same value along all directions. Comment on the nature of this solid. Would it show cleavage property ?

Ans. Since refractive index of the solid has same value in all directions *i.e.,* isotropic, it is an **amorphous solid.** It will not show cleavage property. When cut with a sharp edged tool (knife) it will cut into two pieces with irregular surfaces.

Q.6. Classify the following solids in different categories based on the nature of intermolecular forces operating in them :

Potassium sulphate, tin, benzene, urea, ammonia, water, zinc sulphide, graphite, rubidium, argon, silicon carbide.

Ans. Potassium sulphate : ionic solid, tin : metallic solid, benzene : molecular solid, urea : molecular solid, ammonia : molecular solid, water : molecular solid, zinc sulphide : ionic solid, graphite : covalent solid, rubidium : metallic solid, argon : molecular solid, silicon carbide : covalent solid.

Q.7. Solid A is very hard electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it ?

Ans. Covalent or network solid like quartz (SiO_2), SiC or C (diamond).

Q.8. Ionic solids conduct electricity in molten state but not in solid state. Explain.

Ans. In solid state, the ions are present in fixed positions in the crystal lattice and cannot move when electric field is applied. However, when melted, the well ordered arrangement of the ions in the crystal is destroyed and the ions are in a position to move about when an electric current is applied. Hence, ionic solids conduct electricity in molten state.

Q.9. What type of solids are electrical conductors, malleable and ductile ?

Ans. Metallic solids.

Q.10 Give the significance of lattice point.

Ans. Lattice points represent the positions of the constituent particles (atoms, molecules or ions) in a crystal lattice.

Q.11. Name the parameters that characterize a unit cell.

Ans. A unit cell is characterized by the two types of parameters:

(*i*) Dimensions along the three edges represented as a, b and c.

(*ii*) Angles between edges α (between b and c), β (between a and c) and γ (between a and b).

Hence a unit cell is represented by six parameters a, b, c, α, β, and γ.

Q.12. Distinguish between :

(*i*) Hexagonal and monoclinic unit cell

(*ii*) Face centred and end centred unit cell

Ans. (*i*) Hexagonal unit cell has two edges of equal length ($a = b \neq c$) while monoclinic unit cell has all the three edges of unequal length ($a \neq b \neq c$).

In hexagonal two angles are of 90° and one angle of 120° ($\alpha = \beta = 90$, $\gamma = 120$). In monoclinic, two angles are of 90° but one is not of 90° ($\alpha = \gamma = 90°$, $\beta \neq 90°$).

(*ii*) Face centred unit cell has points at the corners as well as at the centre of each face. It has 4 atoms per unit cell.

End centred unit cell has points at all the corners and at the centre of any two opposite faces. It has 2 atoms per unit cell.

Q.13. Explain how much portion of an atom located at :

(*i*) corner and (*ii*) body centre of a cubic unit cell is part of its neighbouring unit cell ?

Ans. (*i*) 1/8 part of an atom located at corner belongs to neighbouring unit cell

(*ii*) No part.

Q.14. What is the two dimensional coordination number of a molecule in square close packed layer ?

Ans. 4.

Q.15. A compound forms hexagonal close packed structure. What is the total number of voids in 0.5 mol of it ? How many of these are tetrahedral voids ?

Ans. An atom in hcp structure has three voids, one octahedral and two tetrahedral

No. of atoms in 0.5 mol $= 0.5 \times 6.022 \times 10^{23}$

$= 3.011 \times 10^{23}$

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Total number of voids $= 3 \times 3.011 \times 10^{23}$
$= 9.033 \times 10^{23}$
Number of tetrahedral voids $= 2 \times 3.011 \times 10^{23}$
$= 6.022 \times 10^{23}$

Q. 16. A compound is formed by two elements M and N. The element N forms ccp and M atoms occupy 1/3 of tetrahedral voids. What is the formula of the compound ?

Ans. Since N forms *ccp* arrangement, it will have 4 atoms in a unit cell.

Number of N atoms in unit cell = 4

For each atom, there are two tetrahedral voids so that there are 8 tetrahedral voids per unit cell.

$$\text{No. of M atoms} = \frac{1}{3} \times 8 = \frac{8}{3}$$

$$\text{Formula} = M_{8/3}N_4$$

or $= M_2N_3$.

Q. 17. Which of the following lattices has the highest packing efficiency (*i*) simple cubic (*ii*) body centred cubic and (*iii*) hexagonal close packed lattice ?

Ans. The packing efficiencies are :

simple cubic = 52.4%

body centred cubic = 68%

hexagonal close packed = 74%

∴ Hexagonal close packed lattice has highest packing efficiency.

Q.18. An element with molar mass 2.7×10^{-2} kg mol^{-1} forms a cubic unit cell with edge length 405 pm. If the density is 2.7×10^3 kg m^{-3}. What is the nature of the cubic unit cell ?

Ans. Edge length = 405 pm = 405×10^{-12} m

Density of the cell = 2.7×10^3 kgm^{-3}

Molar mass = 2.7×10^{-2} kg mol^{-1}

Now, density $= \dfrac{Z \times M}{a^3 \times N_A}$

Z = ?

$$2.7 \times 10^3 \text{ kg m}^{-3} = \frac{Z \times 2.7 \times 10^{-2} \text{kg mol}^{-1}}{(405 \times 10^{-12}\text{m})^3 \times (6.022 \times 10^{23}\text{mol}^{-1})}$$

$$\therefore Z = \frac{(2.7 \times 10^3 \text{kg m}^{-3}) \times (405 \times 10^{-12}\text{m})^3 \times (6.022 \times 10^{23}\text{mol}^{-1})}{2.7 \times 10^{-2}\text{kg mol}^{-1}}$$

$= 4.0$

Since the unit cell contains 4 atoms, it is **cubic close packed structure, *ccp*.**

Q.19. What type of defect can arise when a solid is heated ? Which physical property is affected by it and in what way ?

Ans. Electronic imperfections.

These defects affect electrical conductivity. It increases with rise in temperature.

Q.20. What type of stoichiometric defect is shown by:

(*i*) ZnS (*ii*) AgBr

Ans. (*i*) ZnS : Frenkel defect.

(*ii*) AgBr : Frenkel defect as well as Schottky defect.

Q.21. Explain how vacancies are introduced in an ionic solid when a cation of higher valence is added as an impurity in it ?

Ans. When a cation of higher valence is added to an ionic solid, it results into impurity defect and cationic vacancies are introduced to maintain electrical neutrality. For example, when molten NaCl is allowed to crystallise in the presence of $SrCl_2$, some of the Na^+ ions are replaced by Sr^{2+} ions. Each Sr^{2+} ion replaces two Na^+ ions to maintain electrical neutrality. One of the site is occupied by Sr^{2+} ion and the other site remains vacant. Hence, cationic vacancies are produced equal to the number of Sr^{2+} ions.

Q.22. Ionic solids which have anionic vacancies due to metal excess defect develop colour. Explain with the help of a suitable example.

Ans. When crystals of alkali metal halides such as NaCl are heated in the atmosphere of sodium vapour, the excess of sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface and combine with sodium atoms to form NaCl. This happens by the loss of electrons by Na atoms to form Na^+ ions. The released electrons diffuse into the crystal and occupy anionic sites. As a result, the structure has an excess of sodium.

The crystals acquire yellow colour because when visible light falls on the crystals, they absorb energy from the visible region to excite the electrons. Hence, they are coloured. Similarly, excess of Li makes LiCl crystals pink and excess of K makes KCl crystals violet.

Q.23. A group 14 element is to be converted into *n*-type semiconductor by doping with a suitable impurity. To which group should this impurity belong ?

Ans. Group 15

e.g., P, As.

Q.24. What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic ? Justify your answer.

Ans. Ferromagnetic substances. When the substance is placed in a magnetic field, all the domains get oriented in the direction of the magnetic field.

NCERT Textbook Exercises

Q.1. Define the term 'amorphous'. Give a few examples of amorphous solids.

Ans. A solid is said to be amorphous if the constituent particles are not arranged in any regular fashion. They may have short range order. For example, glass, plastics, amorphous silica.

Q.2. What makes a glass different from a solid such as quartz ? Under what conditions could quartz be converted into glass ?

Ans. Quartz is a crystalline solid in which SiO_4 tetrahedral units are arranged in an orderly arrangement. Glass is a supercooled liquid and is an amorphous solid.

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In which SiO_4 tetrahedral units are not arranged in any regular order.

Quartz can be converted into glass by melting the quartz and then cooling it rapidly.

Q.3. Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous.

(*a*) Tetra phosphorus decoxide (P_4O_{10})

(*b*) Graphite (*c*) Brass

(*d*) Ammonium phosphate $(NH_4)_3PO_4$

(*e*) SiC (*f*) Rb (*g*) I_2 (*h*) LiBr (*i*) P_4

(*j*) Si (*k*) Plastic

Ans. *Refer Solved Example 2 (Page 8).*

Q.4. (*a*) What is meant by term 'coordination number' ?

(*b*) What is the coordination number of atoms :

(*i*) in a cubic close packed structure

(*ii*) in a body centred cubic structure.

Ans. (*a*) Coordination number gives the number of nearest neighbours with which a given atom is in contact. In case of ionic crystals, coordination number of an ion in the crystal is the number of oppositely charged ions surrounding that ion.

(*b*) (*i*) 12 (*ii*) 8

Q.5. How can you determine the atomic mass of an unknown metal if you know its density and the dimension of its unit cell ? Explain.

Ans. *Refer Text ; page 35.*

$$\text{Atomic mass, } M = \frac{\rho \times a^3 \times N_A}{Z}$$

Q.6. 'Stability of a crystal is reflected in the magnitude of its melting points'. Comment. Collect melting points of solid water, ethyl alcohol, diethyl ether and methane from a data book. What can you say about the inter-molecular forces between these molecules ?

Ans. The melting point of a crystal depends upon the magnitude of forces holding the constituent particles together, which determine the stability. Higher the melting point, greater are the forces holding the constituent particles together and hence greater is the stability. For example, ionic crystals such as NaCl, KNO_3, etc. have very high melting points and are stable. On the other hand, molecular solids such as naphthalene, iodine, etc. are less stable because they have low values of melting points.

The melting points of some compounds are :

Water = 273 K, ethyl alcohol = 155.8 K, diethyl ether = 156.8 K and methane = 90.5 K.

The intermolecular forces in water and ethyl alcohol are mainly hydrogen bonding. The higher melting point of water than ethyl alcohol indicates that the hydrogen bonding in water is stronger than in ethyl alcohol. Diethyl ether is a polar molecule and, therefore, the intermolecular forces in diethyl ether are dipole-dipole interactions. On the other hand, methane is a non-polar molecule and the only forces present in them are the weak van der Waals forces (London dispersion forces). These are weaker than dipole-dipole interactions and hence methane has very low melting point than diethyl ether.

Q.7. How will you distinguish between the following pair of terms :

(*i*) Hexagonal close packing and cubic close packing

(*ii*) Crystal lattice and unit cell.

(*iii*) Tetrahedral void and octahedral void.

Ans. (*i*)

Hexagonal close packing	Cubic close packing
(*i*) In *hcp*, the spheres of the third layer are exactly aligned with those of the first layer. This arrangement is represented as AB AB..... type.	(*i*) In *ccp*, the spheres of the third layer are not aligned with those of the first layer or second layer. The layers of fourth layer are aligned with those of the first layer. This pattern is represented as ABCABC .....
(*ii*) In *hcp*, the tetrahedral voids of the second layer may be covered by the spheres of the third layer.	(*ii*) In *ccp*, the third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids.

(*ii*) The three dimensional arrangement of constituent particles of a substance (atoms, ions or molecules) is called crystal lattice.

The smallest repeating pattern in a crystal lattice which when repeated in three dimensions gives the crystal is called unit cell.

(*iii*) A void surrounded by four spheres is called a tetrahedral void while a void surrounded by six spheres is called an octahedral void.

Q.8. How many lattice points are there in one unit cell of each of the following lattice ?

(*a*) face centred cubic (*b*) face centred tetragonal (*c*) body centred.

Ans. (*a*) In face centred cubic arrangement, number of lattice points are :

8 (at corners) + 6 (at face centres)

$$\text{Lattice points per unit cell} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

(*b*) In face centred tetragonal, number of lattice points are:

= 8 (at corners) + 6 (at face centres)

$$\text{Lattice points per unit cell} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

(*c*) In body centred cubic arrangement number of lattice points are :

= 8 (at corners) + 1 (at body center)

$$\text{Lattice points per unit cell} = 8 \times \frac{1}{8} + 1 = 2$$

Q.9. Explain : (*a*) The basis of similarities and differences between metallic and ionic crystals.

(*b*) Ionic solids are hard and brittle.

Ans. (*a*) Basis of similarities

(*i*) Both ionic and metallic crystals have electrostatic forces of attraction. In ionic crystals, these are between the oppositely charged ions while in metals, these are among the valence electrons and the kernels. That is why both ionic and metallic crystals have high melting points.

(*ii*) In both cases, the bond is non-directional.

Basis of differences

(*i*) In ionic crystals, the ions are not free to move and therefore, they do not conduct electricity in the solid state. They conduct electricity in the molten state or in their aqueous solution. However, in metals, the valence electrons are free to move and hence they conduct electricity in the solid state.

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(*ii*) Ionic bond in ionic crystals is strong due to electrostatic forces of attraction. However, metallic bond may be weak or strong depending upon the number of valence electrons and the size of the kernels.

(***b***) Ionic crystals are hard because there are strong electrostatic forces of attraction among the oppositely charged ions. They are brittle because the ionic bond is non-directional.

Q.10. Calculate the efficiency of packing in case of a metal crystal for

(*a*) simple cubic (*b*) body centered cubic (*c*) face centered cubic

(with the assumptions that atoms are touching each other).

Ans. *Refer Text ; page 22–24.*

Q.11. Silver crystallizes in *fcc* lattice. If edge length of the cell is 4.077×10^{-8} cm and density is 10.5 g cm^{-3}. Calculate the atomic mass of silver.

(A.I.S.B. 2008, Uttarakhand S.B. 2015)

Ans. Density, $\rho = \dfrac{Z \times M}{a^3 \times N_A}$

or $M = \dfrac{\rho \times a^3 \times N_A}{Z}$

$Z = 4$ (*fcc* lattice), $\rho = 10.5$ g cm^{-3}, $N_A = 6.022 \times 10^{23}$, ($a = 4.077 \times 10^{-8}$ cm)

$$\therefore \quad M = \frac{10.5 \times (4.077 \times 10^{-8})^3 \times 6.022 \times 10^{23}}{4}$$

$$= 107.12 \text{ g mol}^{-1}.$$

Q.12. A cubic solid is made of two elements P and Q. Atoms of Q are at the corners of the cube and P at the body centre. What is the formula of the compound ? What are the coordination numbers of P and Q ?

Ans. As atoms Q are present at the 8 corners of the cube, therefore, number of atoms of Q in the unit cell = $8 \times \frac{1}{8} = 1$

As atoms P are present at the body centre, therefore, number of atoms P in the unit cell = 1

$\therefore$ Formula of the compound = PQ

Coordination number of each P and Q = 8

Q.13. Niobium crystallizes in body centered cubic structure. If density is 8.55 g cm^{-3}, calculate atomic radius of niobium using its atomic mass 93 u.

Ans. *Refer Solved Example 27 (Page 38).*

Q.14. If the radius of the octahedral void is *r* and radius of the atoms in close packing is R. Derive relation between *r* and R.

Ans. *Refer Text ; page 24–25.*

Q.15. Copper crystallizes into a *fcc* latice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.29 g cm^{-3}.

Ans. Density, $\rho = \dfrac{Z \times M}{a^3 \times N_A}$

For *fcc* lattice, $Z = 4$

Atomic mass, M of copper = 63.5

$$a = 3.61 \times 10^{-8} \text{ cm}$$

$$\therefore \quad \rho = \frac{4 \times 63.5}{(3.61 \times 10^{-8})^3 \times 6.022 \times 10^{23}} = \mathbf{8.96 \text{ g cm}^{-3}}$$

This value is close to measured value.

Q.16. Analysis shows that nickel oxide has formula $Ni_{0.98}O_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions ?

Ans. *Refer Solved Example 34 (Page 46).*

Q.17. What is a semiconductor ? Describe the two main types of semiconductors and contrast their conduction mechanism.

Ans. The substances whose conductance lies between that of conductors (metals) and insulators are called semiconductors. They have conductivity values ranging from 10^{-6} to $10^4 \Omega^{-1}m^{-1}$. Two main types of semi-conductors are *n*-type and *p*-type. *For details Refer Text, page 51-52.*

Q.18. Non-stoichiometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2 : 1. Can you account for the fact that this substance is a *p*-type semi-conductor ?

Ans. Since the ratio of Cu : O in Cu_2O is less than 2 : 1, therefore, Cu_2O is non-stoichiometric crystal. This means that some Cu^+ ions have been replaced by Cu^{2+} ions. To maintain electrical neutrality, every two Cu^+ ions will be replaced by one Cu^{2+} ion thereby creating a hole. Since the conduction will be due to the presence of these positive holes, it is a *p*-types semi-conductor.

Q.19. Ferric oxide crystallizes in a hexagonal close packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.

Ans. In a close packed arrangement, there is one octahedral site corresponding to each atom constituting the lattice.

No. of oxide ions per unit cell in *hcp* arrangement = 6

No. of octahedral holes = 6

No. of ferric ions = $6 \times \frac{2}{3} = 4$

Formula of the compound Fe_4O_6 or Fe_2O_3.

Q.20. Classify each of the following as being either a *p*-type or a *n*-type semiconductor :

(*i*) Ge doped with In (*ii*) B doped with Si

Ans. (*i*) Ge belongs to group 14 and In belongs to group 13.

Therefore, an electron deficient hole is created and its is a ***p*-type semiconductor.**

(*ii*) B belongs to group 13 and Si belongs to group 14. Therefore, there will be a free electron and it is a ***n*-type semi conductor.**

Q.21. Gold (atomic radius = 0.144 nm) crystallizes in a face centered unit cell. What is the length of a side of the cell.

Ans. For face centred unit cell, radius of atom

$$r = \frac{a}{2\sqrt{2}}$$

or $$a = 2r\sqrt{2}$$

$$r = 0.144 \text{ nm}$$

$$\therefore \quad a = 2 \times 0.144 \times 1.414 = \mathbf{0.407 \text{ nm}}.$$

Q.22. In terms of band theory, what is the difference (*i*) between a conductor and an insulator (*ii*) between a conductor and a semi-conductor ?

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Ans. (*i*) The energy gap between the valence band and the conduction band in an insulator is very large. As a result, under an applied electric field, the electrons cannot jump from valence band to conduction band and therefore, such a substance has very small conductivity and behaves as an insulator. On the other hand, in a conductor the energy gap is either very small or there is overlapping between valence band and conduction band. Therefore, under an applied electric field, the electron can jump from valence band to insulator band and the substance shows conductivity.

(*ii*) In a conductor, the energy gap between valence band and conductance band is very small or there is overlapping between valence band and conduction band. But in a semi-conductor, there is always a small energy gap between them. (*see Fig. 54 on page 50*).

Q.23. Explain the following terms with suitable examples :

(*i*) Schottky defect (*ii*) Frenkel defect

(*iii*) Interstitials (*iv*) F-centres

Ans. *Refer Text pages 42, 43, 44.*

Q.24. Aluminium crystallizes in a cubic close packed structure. Its metallic radius is 125 pm.

(*a*) What is the length of the side of the unit cell ?

(*b*) How many unit cells are there in 1.00 cm^3 of aluminium ?

Ans. *Refer Solved Example 29 (Page 38).*

Q.25. If NaCl is doped with 10^{-3} mol% of $SrCl_2$. What is the concentration of cation vacancies ?

Ans. *Refer Solved Example 33 (Page 46).*

Q.26. Explain the following with suitable examples :

(*a*) ferromagnetism (*b*) paramagnetism

(*c*) ferrimagnetism (*d*) antiferromagnetism

(*e*) 12–16 and 13–15 group compounds.

Ans. *Refer Text page 53-54 [for (a) to (d)].*

(*e*) The solid binary compounds prepared by combining elements of group 12 and 16 are called 12 – 16 compounds. For example, CdS, ZnS, etc. The compounds prepared by combining elements of group 13 and 15 are called 13–15 compounds. For example, AlP, GaAs, etc. These compounds are used as semiconductors.

NCERT Exemplar Problems

Subjective Questions

Objective Questions from Exemplar Problems are given in Competition File, page 90.

Short Answer Type Questions

1. Why are liquids and gases categorised as fluids?

Ans. The liquids and gases have a property to flow i.e. the molecules of liquids and gases can easily move past and tumble over one another freely. Because of their tendency to flow, these have been categorised as fluids.

2. Why are solids incompressible?

Ans. The internuclear distances between the constituent particles (atoms, molecules or ions) in solids are very less. On bringing them further closer, there will be large repulsive forces between electron clouds of these particles. Therefore, solids cannot be compressed.

3. Inspite of long range order in the arrangement of particles why are the crystals usually not perfect?

Ans. During the crystallisation process, some deviations from the ideal ordered arrangement may occur. As a result, crystals are usually not perfect.

4. Why does table salt, NaCl, some times appear yellow in colour?

Ans. The yellow colour of sodium chloride crystals is due to metal excess defect. In this defect, the unpaired electrons get trapped in anion vacancies. These sites are called F-centres. The yellow colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals.

5. Why is FeO(*s*) not formed in stoichiometric composition?

Ans. In the crystals of FeO, some of the Fe^{2+} cations are replaced by Fe^{3+} ions. To balance the charge, three Fe^{2+} ions are replaced by two Fe^{3+} ions to make up for the loss of positive charge. As a result, there would be less amount of metal as compared to stoichiometric proportion.

6. Why does white ZnO (s) becomes yellow upon heating?

Ans. When ZnO is heated it loses oxygen as :

$$ZnO \xrightarrow{Heat} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

The Zn^{2+} ions are entrapped in the interstitial sites and electrons are entrapped in the neighbouring interstitial sites to maintain electrical neutrality. This results in metal excess defect and F-centres are created. Due to the presence of electrons in the interstitial voids, the colour is yellow.

7. Why does the electrical conductivity of semiconductors increase with rise in temperature?

Ans. According to band model, the gap between conduction band and valence band is small in semiconductors as shown in Fig. 54 (Page 51).

Therefore, electrons from the valence band can jump to the conduction band on increasing temperature. Thus, they become more conducting as the temperature increases.

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8. Explain why does conductivity of germanium crystals increase on doping with gallium.

Ans. On doping germanium with gallium, some of the positions of lattice of germanium are occupied by gallium. Gallium atom has only three valence electrons. Therefore, fourth valency of nearby germanium atom is not satisfied and this site remains vacant. This place is deficient of electrons and is called electron hole or electron vacancy. Electron from neighbouring atom moves to fill the gap, thereby creating a hole in its original position. Under the influence of electric field, electrons move towards positively charged plates through these holes and conduct electricity. The holes appear to move towards negatively charged plates. The movement of electrons (or electron holes) results in increase in conductivity of germanium.

9. In a compound, nitrogen atoms (N) make cubic close packed lattice and metal atoms (M) occupy one-third of the tetrahedral voids present. Determine the formula of the compound formed by M and N?

Ans. N atoms make up ccp arrangement and there are two tetrahedral sites per atom of N.

No. of N atoms per unit cell = 4

No. of tetrahedral sites = $4 \times 2 = 8$

No. of sites occupied by M = $\frac{1}{3} \times 8 = \frac{8}{3}$

$\therefore$ No. of M atoms per unit cell = $\frac{8}{3}$

Formula $M_{8/3}N_4$ or M_8N_{12} or M_2N_3

10. Under which situations can an amorphous substance change to crystalline form?

Ans. On heating, amorphous solids become crystalline at some temperature. For example, some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation.

QUICK MEMORY TEST

A. Say True or False

1. Tetragonal and orthorhombic crystal systems have same axial angles.
2. In a *fcc* unit cell, the distance along one of the faces of the unit cell is 2.828 times the radius of the atoms.
3. In a face centred cubic system, number of atoms at faces is 4.
4. Copper crystallises in a *fcc* lattice. If radius of copper atom is 130 pm, then the edge length of the unit cell will be 450.32 pm.
5. The percentage of vacant space in *bcc* unit cell and simple cubic unit cell are 26% and 32% respectively.
6. Number of atoms per unit cell in *fcc* and *bcc* unit cells are 4 and 2 respectively.
7. For *bcc* metallic unit cell, the edge length (a) and radius (r) of atom are related as : $a = \frac{4}{\sqrt{3}} r$.
8. The volume of a *fcc* unit cell with atomic radius of atom 100 pm is 2.26×10^{-29} m^3.
9. The two ions A^+ and B^- have radii 90 and 200 pm respectively. In close packed crystal of a compound AB, the coordination number of A^+ is 4.
10. Number of Na^+ and Cl^- ions in a unit cell are 6 and 6 respectively.
11. Schottky defect results in the decrease in the density of the crystal.
12. Number of octahedral voids in 1 mole of a compound having *ccp* and *bcc* arrangement are 24.08×10^{23} and 12.04×10^{23} respectively.
13. The edge length of an ionic crystal XY having sodium chloride type structure is the sum of the radius of P and Q.
14. *hcp* arrangement has 6 atoms per unit cell.
15. Ferromagnetic and antiferromagnetic solids change into paramagnetic at high temperature.

B. Complete the missing links

1. The number of atoms for primitive unit cell is ....., for body centred cubic unit cell is ..... and for face centred cubic unit cell is ..... .
2. The electrical conductivity of metals ..... with decrease in temperature.
3. The substances which are strongly attracted by the magnetic field and show permanent magnetism even when magnetic field is removed are called ..... substances.
4. The formula of a compound is ..... in which atoms of element B form *hcp* lattice and those of the element A occupy 2/3rd of tetrahedral voids.
5. A group 14 element is to be converted in to *n*-type semiconductor by doping it with a suitable impurity belonging to group ..... of the periodic table.
6. If electrical conductivity is found to be same in all directions through a solid, the substance is ..... and this property is called ..... .
7. The coordination number of each sphere in hcp is ....., in *ccp* is ..... and in *bcc* packing is ..... .
8. The packing fraction of a simple unit cell is ..... .
9. The empty space in *hcp* is ..... and that in *bcc* packing is ..... .
10. In a body centred cubic crystal, the nearest neighbour distance is ..... times the edge of the crystal and in a face centred cubic crystal, the nearest neighbour distance is ..... times the edge of the crystal.
11. An octahedral void is ..... times larger than a tetrahedral void.
12. In a body centred cubic arrangement ..... atoms along the body diagonal touch each other.

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13. The compound showing both Frenkel and Schottky defects is ..... .
14. If there is a large energy gap between the filled valence band and empty conduction band, the substance acts as ..... .
15. In a body centred cubic crystal of an element, the ratio of edge of the unit cell to the radius of the atom is ..... .
16. NaCl crystals have yellow colour due to the presence of ..... .

C. Choose the correct alternative

1. Lithium, sodium, potassium and rubidium crystallize in the *bcc / fcc* structure.
2. Most unsymmetrical crystal system is *monoclinic / triclinic*.
3. Orthorhombic has *4 / 3* types of lattices.
4. Total number of tetrahedral and octahedral voids in *hcp* arrangement are *12 / 18*.
5. In a crystalline solid, anions B are arranged in a ccp. Cations A are equally distributed between octahedral and tetrahedral voids. If all the octahedral voids are oocupied, the formula of the compound is A_2B / A_3B.
6. In a body centred cubic unit cell of elements, the radius of an atom is *0.433 / 0.354* times the edge length of the unit cell.
7. For a hcp unit cell, the number of atoms per unit cell is *6 / 4*.
8. $CdCl_2$ added to AgCl crystal will introduce *Schottky defect / Frenkel defect*.
9. MnO_2 is *antiferromagnetic / ferromagnetic* substance.
10. *Ferrimagnetism / ferromagnetism* arises due to unequal number of domains in opposite direction resulting in net magnetic moment.
11. The substance showing both Schottky defect and Frenkel defect is *AgBr / ZnS*.
12. When silicon is doped with arsenic, *n-type/p-type* semiconductor is produced.

Answers QUICK MEMORY TEST

A. Say True or False

1. **True.** Both have axial angles $\alpha = \beta = \gamma = 90°$.
2. **True.** In *fcc* unit cell, the face diagonal is
$$4r = \sqrt{2}.a$$
or $$a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}\, r$$
$$= 2 \times 1.414\, r = 2.828\, r$$
3. **False.** No. of atoms at faces = 3
4. **False.** Edge length $(a) = 2\sqrt{2}\, r$
$$= 2 \times 1.414 \times 130 = 367.64 \text{ pm}$$
5. **False.** In *bcc* vacant space = 32% and in simple cubic unit cell vacant space = 48%.
6. **True.** 7. **True.**
8. **True.** For *fcc* arrangement, $r = \frac{a}{2\sqrt{2}}$
$$a = 2\sqrt{2}\,.\,r = 2 \times 1.414 \times 100 \times 10^{-12} \text{ m}$$
$$= 2.828 \times 10^{-10} \text{ m}$$
$\therefore$ Volume of unit cell $= a^3 = (2.828 \times 10^{-10}\text{ m})^3$
$$= 2.26 \times 10^{-29}\text{ m}^3$$
9. **False.** $\frac{r(A^+)}{r(B^-)} = \frac{90 \text{ pm}}{200 \text{ pm}} = 0.45$
Since it lies in the range of 0.414 to 0.732, the coordination number of A^+ will be 6.
10. **False.** No. of Na^+ ions = 4, No. of Cl^- ions = 4.
11. **True.**
12. **False.** 1 mole of compound in *ccp* or *bcc* arrangement has 6.02×10^{23} atoms.
No. of octahedral voids in *ccp* or *bcc* arrangement $= 6.023 \times 10^{23}$
13. **False.** $d(XY) = 2(r_{X+} + r_{Y-})$
14. **True.** 15. **True.**

B. Complete the missing links

1. 1, 2, 4
2. increases
3. ferromagnetic
4. A_4B_3
5. 15
6. amorphous, isotropy
7. 12, 12, 8
8. 52.4%
9. 26%, 32%
10. $\frac{\sqrt{3}}{2}(0.866), \frac{1}{\sqrt{2}}(0.707)$
11. 0.414/0.225 = 1.84
12. three
13. AgBr
14. insulator
15. $\frac{a}{\sqrt{3}\,a/4} = \frac{4}{\sqrt{3}} = (2.309)$
16. F-centres

C. Choose the correct alternative

1. *bcc*
2. triclinic
3. 4
4. 18
5. A_2B
6. 0.433
7. 6
8. Schottky defect
9. antiferromagnetic
10. ferrimagnetism
11. AgBr
12. *n*-type

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HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. Diamond and solid rhombic sulphur both are covalent solids but the latter has very low melting point than the former. Explain why ?

Ans. Diamond is a three dimensional network covalent solid having very strong interatomic forces while, rhombic sulphur is a molecular solid consisting of puckered eight membered rings (S_8) held together by weak van der Waals' forces.

Q.2. Why does the window glasses of the old buildings look milky ?

Ans. Due to heating during the day and cooling at night (*i.e.*, annealing) over a number of years, glass acquires some crystalline character and hence looks milky.

Q.3. Can cubic lattice have end-centred unit cell ?

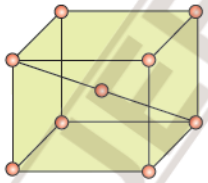
Ans. No, because a cubic unit cell must have all the faces to be same.

Q.4. Silver iodide crystallizes in the cubic close packed zinc sulphide structure. Assuming that ions occupy the lattice points, what fraction of the tetrahedral sites is occupied by Ag^+ ions ?

Ans. To maintain stoichiometry, Ag^+ ions occupy half the tetrahedral sites because there are two tetrahedral sites occupied for each I^- ion.

$\therefore$ 50% tetrahedral sites are occupied.

Q.5. An element 'X' has *bcc* lattice as shown below : The unit cell length, *a* is 306 pm.



(*a*) What is the distance between nearest neighbours ?

(*b*) What is the distance between next nearest neighbours ?

(*c*) How many nearest neighbours does each X atom have ?

(*d*) How many next nearest neighbours does each X have ?

Ans. (*a*) The body diagonal is $\sqrt{3}\,.\,a = 1.732 \times 306 = 530$ pm

Nearest neighbours along body diagonal are half the body diagonal.

$\therefore$ Distance between nearest neighbours $= \dfrac{530}{2} = 265$ pm

(*b*) The next nearest neighbours are along the edge.

$\therefore$ Distance between next nearest neighbour = 306 pm

(*c*) 8, because the body centre is next to 8 corners.

(*d*) 6, because each corner has neighbours along each edge.

Q.6. For a cubic crystal, the face diagonal is 4.25Å. Calculate its face length.

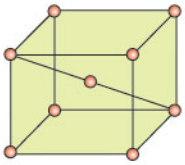
Ans. If a is the length of the face, then

$$\text{face diagonal} = \sqrt{a^2 + a^2} = \sqrt{2}a$$

$$\therefore \text{Face length}, \quad a = \frac{\text{Face diagonal}}{\sqrt{2}} = \frac{4.25}{1.414} = \mathbf{3.01\text{Å}}$$

Q.7. What fraction of edge is not covered by atoms in *bcc* arrangement ?

Ans. If a is the edge length of *bcc* unit cell and r is the radius of atom, then



$$\text{edge not covered by atoms} = a - 2r$$

$$\text{In bcc, body diagonal} = \sqrt{3}\,a$$

$$4r = \sqrt{3}\,a \quad \text{or} \quad r = \frac{\sqrt{3}}{4}a$$

$$\therefore \text{Edge not covered by atoms} = a - 2 \times \frac{\sqrt{3}}{4}a$$

$$= \frac{a\left(\dfrac{2-\sqrt{3}}{2}\right)}{a} = \frac{2 - 1.732}{2} = \mathbf{0.134\%}$$

Q.8. A face centred cubic lattice of a single type of atoms has same defects and its one corner and one face centre is left unoccupied per unit cell. Calculate the packing fraction of such solid.

Ans. Suppose the edge length of unit cell is a and radius of each atom is r.

$$\text{No. of atoms per unit cell} = 7 \times \frac{1}{8} + 5 \times \frac{1}{2} = \frac{27}{8}$$

$$\text{For face centred unit cell,} \quad a = 2\sqrt{2}\,r$$

$$\text{Volume of unit cell,} \quad a^3 = (2\sqrt{2}\,r)^3 = 16\sqrt{2}\,r^3$$

$$\text{Total volume of } \frac{27}{8} \text{ atoms} = \frac{27}{8} \times \frac{4}{3}\pi r^3 = \frac{9}{2}\pi r^3$$

$$\text{Packing fraction} = \frac{\dfrac{9}{2}\pi r^3}{16\sqrt{2}\,r^3}$$

$$= \frac{9\pi}{32\sqrt{2}} = \frac{9 \times 3.142}{32 \times 1.414}$$

$$= \mathbf{0.625}$$

Q.9. The CsCl has cubic structure of Cl^- ions in which Cs^+ ion is present in the body centre of the cube. Its density is 3.99 g cm^{-3}.

(*i*) Calculate the length of the edge of unit cell.

(*ii*) What is the distance between Cs^+ and Cl^- ions?

(*iii*) What is the radius of Cs^+ ion if the radius of Cl^- ion is 180 pm ?

Ans. The unit cell of CsCl has cubic arrangement of Cl^- ions and Cs^+ ion is present in the body centre of the cube. Therefore, the unit cell contains one Cs^+ and one Cl^- ion or one CsCl unit, *i.e.*, Z = 1

Molar mass of CsCl, M = 133 + 35.5 = 168.5 g mol^{-1}

$$\text{Density}, \rho = \frac{Z \times M}{a^3 \times N_A}$$

$$3.99\ \text{g cm}^{-3} = \frac{1 \times (168.5\ \text{g mol}^{-1})}{a^3 \times (6.022 \times 10^{23}\ \text{mol}^{-1})}$$

$$a^3 = \frac{1 \times (168.5\ \text{g mol}^{-1})}{(3.99\ \text{g cm}^{-3}) \times (6.022 \times 10^{23}\ \text{mol}^{-1})}$$

$$= 7.02 \times 10^{-23}\ \text{cm}^3$$

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(*i*) Let length of the edge of unit cell = a

$$a^3 = 7.02 \times 10^{-23}\ cm^3 = 70.2 \times 10^{-24}\ cm^3$$

$$a = (70.2 \times 10^{-24}\ cm)^{1/3}$$

$$= 4.12 \times 10^{-8}\ cm = \mathbf{412\ pm}$$

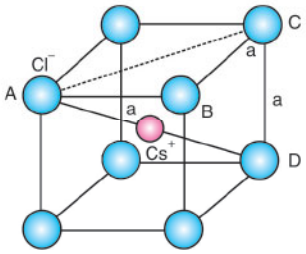
(*ii*) As shown in the figure, Cs^+ ion is present in the centre of unit cell and is in contact with 8 Cl^- ions at the corners. It is clear that the length of the body diagonal is equal to twice the distance between centre of Cs^+ and centre of Cl^- ion. The body diagonal can also be calculated as :

If length of unit cell edge is a, then face diagonal AC, is

$$AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}\,a$$

The body diagonal AD is :

$$AD = \sqrt{AC^2 + CD^2} = \sqrt{2a^2 + a^2} = \sqrt{3}\,a$$



Now,

$$2\,(\text{Distance between } Cs^+ \text{ and } Cl^-) = \sqrt{3}\,a$$

or $$\text{Distance between } Cs^+ \text{ and } Cl^- = \frac{\sqrt{3}}{2}a$$

$$= \frac{\sqrt{3}}{2} \times 412\ pm = 1.732 \times 206\ pm$$

$$= \mathbf{356.8\ pm.}$$

(*iii*) Let the radius of Cl^- be $r(Cl^-)$ so that

$$r(Cs^+) + r(Cl^-) = 356.8\ pm$$

$$r(Cl^-) = 356.8 - 180 = \mathbf{176.8\ pm.}$$

Q.10. A metal crystallizes into two cubic phases, face centred cubic (*fcc*) and body centred cubic (*bcc*), whose unit cell lengths are 3.5 Å and 3.0 Å respectively. Calculate the ratio of densities of *fcc* and *bcc*.

Ans. Density of a crystal is

$$d = \frac{Z \times \text{Formula mass of substance}}{N_A \times a^3}$$

Now, for *fcc*, Z = 4 and for *bcc*, Z = 2

$$\therefore \quad d(fcc) = \frac{Z \times \text{Formula mass of substance}}{N_A \times (305\ \text{Å})^3}$$

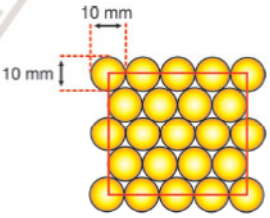
$$d(bcc) = \frac{2 \times \text{Atomic mass of metal}}{N_A \times (3.0\ \text{Å})^3}$$

$$\therefore \quad \frac{d(fcc)}{d(bcc)} = \frac{4}{2} \times \frac{(3.0)^3}{(3.5)^3} = \mathbf{1.26.}$$

Q.11. You are given marbles of diameter 10 mm. They are to be placed such that their centres are lying in a square bound by four lines each of length 40 mm. What will be the arrangement of marbles in a plane so that maximum number of marbles can be placed inside the area ? Sketch the diagram and derive an expression for the number of molecules per unit area. ***(I.I.T. 2003)***

Ans. Area of square = 40 × 40 = 1600 mm^2

To have maximum number of spheres, packing must be *hcp*. As shown in the figure, the maximum number of spheres of diameter 10 mm are = 18



Area = 1600 mm^2 = 16 cm^2

∴ No. of spheres per cm^2

$$= \frac{18}{16} = \mathbf{1.125}$$

Q.12. A compound AB has rock salt type structure. The formula weight of AB is 6.023 Y amu and the closest A—B distance is $Y^{1/3}$ nm, where Y is an arbitrary number.

***(a)* Find the density of the lattice.**

(b)* If the density of lattice is found to be 20 kg m^{-3}, predict the type of defect.** ***(I.I.T. 2004)

Ans. (*a*) Density of a crystal is

$$d = \frac{Z \times \text{Formula mass of substance}}{N_A \times a^3}$$

Now AB has rock salt type structure *i.e.*, *fcc* so that

$$Z = 4$$

Formula mass = 6.023 Y × 10^{-3} kg, $a = 2Y^{1/3}$ nm = $2Y^{1/3} \times 10^{-9}$ m

$$\therefore \quad \text{Density} = \frac{4 \times 6.023\ Y \times 10^{-3}\ kg}{6.023 \times 10^{23} \times (2Y^{1/3} \times 10^{-9}\ m)^3}$$

$$= \mathbf{5.0\ kg\ m^{-3}.}$$

(*b*) Since the observed density (20 kg m^{-3}) is higher than the calculated value (5 kg m^{-3}), the compound must has either interstitial impurity defect or substitutional impurity defect.

Revision Exercises

Very Short Answer Questions *Carrying 1 mark*

1. Crystalline solids are anisotropic in nature. What does this statement mean? *(D.S.B. 2011)*
2. Define a unit cell. How many atoms are present in a simple cubic unit cell ?
3. In a close packed arrangement of N spheres, how many (*i*) tetrahedral and (*ii*) octahedral sites are present ?
4. Why is Frenkel defect not found in pure alkali metal halides ?
5. What is the coordination number of *hcp* and *ccp* structures ? *(Jammu S.B. 2015)*
6. State the type of crystal defects shown by AgBr. *(Meghalaya S.B. 2017)*
7. What is meant by point defects in crystals? *(Jharkhand S.B. 2011)*

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8. What is meant by 'doping' in a semiconductor ? (*D.S.B. 2012*)
9. What is the radius ratio (r^+/r^-) for an ion to occupy tetrahedral site ?
10. Explain the nature of crystal defect produced when sodium crystal is doped with $MgCl_2$?
11. What is the effect of Frenkel structural defect on the electrical conductivity of a crystalline solid?
12. Why does Frenkel defect not change the density of AgCl crystals?
13. What makes alkali metal halides sometimes coloured, which are otherwise colourless ? (*D.S.B. 2004*)
14. What is meant by coordination number? (*Uttarakhand S.B. 2014*)
15. How does temperature influence the conductivity of a semi-conductor ? (*Pb.S.B. 2007*)
16. What type of substances exhibit anti-ferromagnetism? (*D.S.B. 2008*)
17. Name an element with which silicon should be doped to given *n*-type of semiconductor. (*D.S.B. 2008C*)
18. How does electrical conductivity vary in metals with temperature? (*Pb.S.B. 2008*)
19. What is the relationship between the edge length (a) of the unit cell and the radius (r) of an atom in a face-centred unit cell? (*Meghalaya S.B. 2013*)
20. Which point defect in crystals of a solid does not change the density of the solid ?(*D.S.B. 2009, 2010*)
21. How does ferromagnetism arise ? (*Pb.S.B. 2011*)
22. A compound forms *hcp* structure. Calculate the total number of voids in 0.5 mol of it. (*Assam S.B. 2017*)
23. Write a point of distinction between a metallic solid and an ionic solid other than metallic lustre. (*D.S.B. 2012*)
24. How many lattice points are there in one unit cell of each of the following lattices?
    (i) Face centred cubic lattice
    (ii) Body centred cubic lattice. (*Pb.S.B. 2012*)
25. Identify each of the following as being either a *p*-type or *n*-type semiconductor:
    (i) Ge doped with In
    (ii) Si doped with As. (*Pb.S.B. 2012*)
26. How many atoms are there in a unit cell of a metal crystallizing in *fcc* structure ? (*D.S.B. 2013, Meghalaya S.B. 2015, Tripura S.B. 2016*)
27. What type of stoichiometric defect is shown by AgCl? (*D.S.B. 2013*)
28. What type of substances would make better permanent magnets: ferromagnetic or ferrimagnetic? (*D.S.B. 2013*)
29. What is the formula of a compound in which the element *Y* forms *ccp* lattice and atoms of *X* occupy 1/3 of tetrahedral voids ? (*D.S.B. 2015*)
30. What are the coordination number of Na^+ and Cl^- ions in NaCl? (*Nagaland S.B. 2016*)
31. What is Frenkel defect? How does it affect density of the solid? (*Karnataka S.B. 2018*)
32. What is the coordination number of particles present in fcc crystal structure? (*Kerala S.B. 2018*)
33. Which point defect in crystals lowers the density of a crystal? (*A.I.S.B. 2009, Assam S.B. 2013, 2015*)
34. What type of semiconductor is obtained when silicon is doped with arsenic ? (*A.I.S.B. 2010*)
35. What type of interactions hold the molecules together in a polar molecular solid ? (*A.I.S.B. 2010*)
36. Which stoichiometric defect in crystals increases the density of a solid ? (*D.S.B. 2011, A.I.S.B. 2012*)
37. How the conductivity of an intrinsic semiconductor be increased ? (*A.I.S.B. 2012*)
38. What is the formula of a compound in which the element Y forms *hcp* lattice and atoms X occupy 2/3rd of tetrahedral voids ? (*A.I.S.B. 2015*)
39. Analysis shows that FeO has a non-stoichiometric composition with molecular formula $Fe_{0.95}O$. Give reason. (*A.I.S.B. 2018*)

Short Answer Questions *Carrying 2 or 3 marks*

1. How are the solids classified on the basis of bonding in them? Give the constituents and one example of each type. (*J.K.S.B. 2011*)
2. What do you understand by the terms 'space lattice' and 'unit cell' ? (*Pb.S.B. 2015*)
3. Explain with the help of diagrams the structural differences between three types of cubic crystals. (*J.K.S.B. 2011*)
4. What are crystalline solids? Give two examples. (*Hr.S.B. 2017*)
5. What are crystalline and amorphous solids? Give four important differences between crystalline and amorphous solids. (*H.P.S.B. 2005, Pb. S.B. 2013*)
6. Explain :
   (a) Zinc oxide is white but it turns yellow on heating and becomes highly conducting.
   (b) $CdCl_2$ will induce Schottky defect if added to AgCl crystal.
7. If the radius of an octahedral void is r and the radius of atoms in close-packed arrangement is R, derive the relationship between r and R.
8. What is meant by coordination number ? What is the coordination number of atoms in a
   (a) cubic close packed structure
   (b) body centred cubic structure.
9. What is the radius ratio (r^+/r^-) for an ion to occupy :
   (i) tetrahedral void. (ii) octahedral void ?
10. What are the differences between Schottky and Frenkel defects ?(*Pb.S.B. 2013, H.P.S.B. 2013, Hr. S.B. 2013*)
11. Explain the Schottky defects in stoichiometric crystals. What are the important consequences of Schottky and Frenkel defects? (*Uttarakhand S.B. 2012*)
12. Differentiate between *n*-type and *p*-type extrinsic semiconductors.
13. Account for electrical conductivity in ionic compounds having
    (i) metal excess defects (ii) metal deficient defects.

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14. Name the types of semiconductors produced when germanium (Ge) is doped separately with boron (B) and arsenic (As). Which one will be a better semiconductor and why ? (*Manipur S.B. 2014*)

15. (*i*) Explain Schottky defect in sodium chloride crystal.
(*ii*) Explain electric properties of semiconductors on the basis of band theory. (*Uttarakhand S.B. 2014*)

16. (*a*) Calculate the packing efficiency in simple cubic lattice. (*Karnataka S.B. 2018*)
(*b*) What is Frenkel defect ? Give an example. (*Karnataka S.B. 2014*)

17. In terms of band theory, what is the difference between
(*a*) a conductor and an insulator
(*b*) a conductor and a semiconductor.

18. Explain the following :
(*i*) Why is Frenkel defect not found in pure alkali metal halides ? (*Meghalaya S.B.2014*)
(*ii*) Anti-ferromagnetic substances have unpaired electrons but their dipole moment is zero. (*Hr. S.B. 2006*)

19. What are semiconductors? How does electrical conductivity of semiconductors vary with temperature? Give one example of intrinsic semiconductor.

Or

What are paramagnetism and ferromagnetism? What type of substances would make better permanent magnets—ferromagnetic or ferrimagnetic? (*Assam S.B. 2018*)

20. Write two differences between ferromagnetic substances and antiferromagnetic substances. (*Pb.S.B. 2009, 2014*)

21. Explain the following terms :
(*i*) Schottky defects
(*ii*) Frenkel defects (*Uttarakhand S.B. 2015, Jammu S.B. 2016*)

22. Explain the following terms with examples :
(*i*) Metal excess defects
(*ii*) Metal deficiency defects (*Hr. S.B. 2011*)

23. (*a*) What are imperfections in solids ?
(*b*) What are F-centres ? (*H.P.S.B. 2011*)

24. (*a*) Define ferromagnetism and ferrimagnetism.
(*b*) Differentiate between metals, insulators and semiconductors on the basis of band theory. (*Hr.S.B. 2012*)

25. (*a*) Why does Frenkel defect not change the density of AgCl crystals ?
(*b*) Why does electrical conductivity of a semiconductor increases with rise in temperature ? (*Pb.S.B. 2012*)

26. (*i*) What is a semiconductor? Mention two main types of semiconductors.
(*ii*) Sodium crystallizes in a body centred cubic (*bcc*) unit cell. Calculate the approximate number of unit cells in 9.2g of sodium. (Atomic mass of Na = 23*u*) (*Assam S.B. 2013*)

27. (*a*) Give two differences between ferromagnetic and anti-ferromagnetic substances.
(*b*) Tungsten crystallizes in body centred cubic lattice. Calculate the number of unit cells in 1.5 g of tungsten. (At. mass of tungsten = 184*u*) (*Pb. S.B. 2013*)

28. (*a*) A unit cell of sodium chloride has four formula units (number of atoms per unit cell). The edge length of unit cell is 0.564 nm. Find out the density of sodium chloride.
(*b*) Define Frenkel defect and Schottky defect. What is the difference between these two? (*Uttarakhand S.B. 2013*)

29. (*a*) NaCl has fcc structure. Calculate the number of NaCl units in a unit cell of NaCl.
(*b*) Calculate the density of NaCl if edge length of NaCl unit cell is 564 pm. (Molar mass of NaCl = 58.5 g mol^{-1}) (*Kerala S.B. 2013*)

30. (*a*) What type of semiconductor is obtained when silicon is doped with boron?
(*b*) What type of magnetism is shown in the following alignment of magnetic moments?

↑ ↑ ↑ ↑ ↑ ↑

(*c*) What type of point defect is produced when AgCl is doped with $CdCl_2$? (*D.S.B. 2013*)

31. Examine the given defective crystal

A^+	B^-	A^+	B^-	A^+
B^-	O	B^-	A^+	B^-
A^+	B^-	A^+	O	A^+
B^-	A^+	B^-	A^+	B^-

Answer the following questions:
(*i*) What type of stoichiometric defect is shown by the crystal?
(*ii*) How is the density of the crystal affected by this defect ?
(*iii*) What type of ionic substances show such defect ? (*D.S.B. 2014*)

32. Explain the following
(*i*) F-centres
(*ii*) Doping (*H.P.S.B. 2015*)

33. Write any two differences between crystalline and amorphous solids. (*H.P.S.B. 2015, D.S.B. 2017*)

34. Distinguish between crystal lattice and unit cell. (*Hr.S.B. 2015*)

35. (*a*) Briefly discuss Schottky defect and give examples.
(*b*) Calculate the density of copper crystal which crystallises in *fcc* arrangement with edge length of 3.61×10^{-8} cm. (*Hr.S.B. 2015*)

36. Define ferromagnetism and ferrimagnetism. (*Pb.S.B. 2015*)

37. Unit cells can be divided into two categories, primitive and centred unit cells.
(*a*) Differentiate between unit cell and crystal lattice.
(*b*) Calculate the number of atoms per unit cell in the following:
(*i*) body centred cubic unit cell (*bcc*)
(*ii*) face centred cubic unit cell (*fcc*) (*Kerala S.B. 2015*)

38. Calculate packing effciency in simple cubic lattice. (*Karnataka S.B. 2018*)

39. Explain
(*i*) radius ratio (*ii*) unit cells
(*iii*) Ferromagnetism (*iv*) Ferrimagnetism
(*v*) F-centre (*vi*) Doping (*H.P.S.B. 2018*)

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40. (*a*) Defince the following terms:
(*i*) F-centre
(*ii*) Unit cell (*Hr. S.B. 2018*)
(*b*) Explain Schottky defect with an example (*Hr. S.B. 2018*)

41. Differentiate between Schottky and Frenkel defects. (*Pb S.B. 2016*)

42. Differentiate between crystalline and amorphous solids. (*Pb S.B. 2016*)

43. What is Schottky defect? Find out the packing efficiency in a simple cubic lattice. (*Kolkata S.B. 2016*)

44. (*a*) Which of the following is a molecular solid?
(*i*) Diamond (*ii*) Graphite
(*iii*) Ice (*iv*) Quartz
(*b*) Unit cells can be classified into primitive and centred unit cells. Differentiate between primitive and centred unit cells.
(*c*) Presence of excess sodium makes NaCl crystal coloured. Explain on the basis of crystal defects. (*Kerala S.B. 2016*)

45. Write short notes on the following :
(*i*) Schottky defect
(*ii*) Ferromagnetic substances. (*H.P.S.B. 2017*)

46. (a) Based on the nature of intermolecular forces, classify the following solids?
(*i*) SiO_2 (*ii*) Ice
(b) ZnO turns yellow an heating. Why ? (*Kerala S.B. 2018*)

47. Assign reasons for the following :
(*i*) Phosphorus doped silicon is a semiconductor
(*ii*) Schottky defect lowers the density of a solid
(*iii*) Some of the very old objects appear slightly milky instead of being transparent. (*A.I.S.B. 2007*)

48. Explain the following properties with suitable examples:
(*i*) ferromagnetism (*ii*) paramagnetism
(*iii*) ferrimagnetism (*A.I.S.B. 2008*)

49. How do metallic and ionic substances differ in conducting electricity ? (*A.I.S.B. 2009*)

50. Explain how you can determine the atomic mass of an unknown metal if you know its mass, density and the dimensions of unit cell of its crystal. (*A.I.S.B. 2011, Manipur S.B. 2012*)

51. Calculate the packing efficiency of a metal crystal for a simple cubic lattice. (*A.I.S.B.2011*)

52. Account for the following:
(*b*) Schottky defects lower the density of related solids.
(*c*) Conductivity of silicon increases on doping it with phosphorus. (*A.I.S.B. 2013*)

53. (*a*) What change occurs when AgCl is doped with $CdCl_2$?
(*b*) What type of semiconductor is produced when silicon is doped with boron? (*A.I.S.B. 2013*)

54. (*i*) What type of non-stoichiometric point defect is responsible for the pink colour of LiCl ?
(*ii*) What type of stoichiometric defect is shown by NaCl?

Or

How will you distinguish between the following pairs of terms :
(*i*) Tetrahedral and octahedral voids
(*ii*) Crystal lattice and unit cell (*A.I.S.B. 2014*)

55. (*i*) Write the type of magnetism observed when the magnetic moments are oppositely aligned and cancel out each other.
(*ii*) Which stoichiometric defect does not change the density of the crystal ? (*A.I.S.B. 2014*)

56. (*a*) Based on the nature of intermolecular forces, classify the following solids: Benzene, silver.
(*b*) AgCl shows Frenkel defect while NaCl does not. Give reason.
(*c*) What type of semiconductor is formed when Ge is doped with Al ? (*A.I.S.B. 2017*)

57. An element 'X' (At. mass = 40 g mol^{-1}) having f.c.c. structure, has unit cell edge length of 400 pm. Calculate the density of 'X' and the number of unit cells in 4 g of 'X'. ($N_A = 6.022 \times 10^{23}$ mol^{-1}) (*A.I.S.B. 2018*)

Long Answer Questions *Carrying 5 marks*

1. What do you understand by imperfections in solids? Explain stoichiometric defects in solids.

2. Discuss briefly the following properties of solids:
(*i*) electrical properties (*ii*) magnetic properties

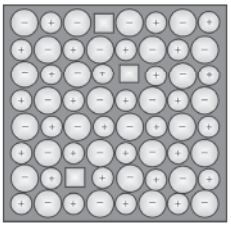
3. (*a*) An element has atomic mass 93 g mol^{-1} and density 11.5 g cm^{-3}. If the edge length of its unit cell is 300 pm, identify the type of unit cell.
(*b*) Write any two differences between amorphous solids and crystalline solids.

OR

(*a*) Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a *fcc* structure. (Atomic mass of Al = 27 g mol^{-1})
(*b*) Give reasons :
(*i*) In stoichiometric defects, NaCl exhibits Schottky defect and not Frenkel defect.
(*ii*) Silicon on doping with phosphorus forms *n*-type semiconductor.
(*iii*) Ferrimagnetic substances show better magnetism than antiferromagnetic substances. (*D.S.B. 2017*)

4. (*i*) Following is the schematic alignment of magnetic moments:

Identify the type of magnetism. What happens when these substances are heated ?
(*ii*) If the radius of the octahedral void is '*r*' and radius of the atoms in close packing is 'R'. What is the relation between '*r*' and 'R'.
(*iii*) Tungsten crystallizes in body centred cubic unit cell. If the edge length of the unit cell is 315.5 pm, what is the radius of tungsten atom?



OR

(*i*) Identify the type of defect shown in the following figure:

What type of substances show this defect ?

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(*ii*) A metal crystallizes in a body centred cubic structure. If '*a*' is the edge length of its unit cell, '*r*' is the radius of the sphere. What is the relationship between '*r*' and '*a*' ?

(*iii*) An element with molar mass 63 g / mol forms a cubic unit cell with edge length of 360.8 p.m. If its density is 8.92 g/ cm^3. What is the nature of the cubic unit cell ? (*CBSE Sample Paper 2017-18*)

NUMERICAL PROBLEMS

1. Potassium iodide has cubic unit cell with cell edge of 705 pm. The density of KI is 3.12 g cm^{-3}. How many K^+ and I^- ions are contained in the unit cell ?

[**Ans.** $4K^+$ and $4I^-$]

2. The unit of an element of atomic mass 96 and density 10.3 g cm^{-3} is a cube with edge length of 314 pm. Find the structure of the crystal lattice (simple cubic, FCC or BCC) (Avogadro's constant, $N_0 = 6.023 \times 10^{23}$ mol^{-1})

[**Ans.** BCC]

3. KCl and NaCl have fcc lattice. Calculate the ratio of density of NaCl to that of KCl if the ratio of edge of NaCl to that of KCl is 0.875. [**Ans.** 1.172]

4. Lithium metal has a body centred cubic structure. Its density is 0.53 g cm^{-3} and its molar mass is 6.94 g mol^{-1}. Calculate the volume of a unit cell of lithium metal.

[**Ans.** 4.35×10^{-23} cm^3]

5. Iron has body centred cubic unit cell edge of 286.65 pm. The density of iron is 7.87 g cm^{-3}. Use this information to calculate Avogadro's number (At. mass of iron = 56 g mol^{-1}) (*D.S.B. 2010*)

6. An element crystallizes in a structure having *fcc* unit cell of an edge 300 pm. Calculate its density if 180 g of this element contains 3.708×10^{24} atoms. (*Pb.S.B. 2012*)

7. An element (density 7.2 g cm^{-3}) crystallizes in a body centred cubic structure having its unit celll edge length 2.88 Å. Calculate the number of atoms present in 156 g of the element. (*Tripura Board 2016*)

8. Silver crystallizes in a fcc lattice. The edge length of its unit cell is 4.07×10^{-8} cm and its density is 10.48 g cm^{-3}. Calculate the relative atomic mass of silver ($N_A = 6.022 \times 10^{23}$ mol^{-1}). (*Kolkata S.B. 2016*)

9. Calculate the distance between Na^+ and Cl^- ions in NaCl crystal if its density is 2.165 g cm^{-3}. (Molar mass of NaCl = 58.5 g mol^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1}).

(*A.I.S.B. 2006*)

10. Iron has a body centred cubic unit cell with a cell edge of 286.65 pm. The density of iron is 7.85 g cm^{-3}. Use this information to calculate Avogadro's number. (*A.I.S.B. 2009*)

11. Silver crystallizes with face centred cubic unit cells. Each side of the unit cell has a length of 409 pm. What is the radius of an atom of silver ? (Assume that each face atom is touching four corner atoms).(*A.I.S.B. 2009*)

12. Tungsten crystallizes in a body centred cubic lattice. Calculate the number of unit cells in 1.5 g of tungsten. Atomic mass of tungsten = 184 u. (*A.I.S.B. 2009*)

13. The well known mineral fluorite is chemically calcium fluoride. It is known that in one unit cell of this mineral there are 4 Ca^{2+} ions and 8 F^- ions and that Ca^{2+} ions are arranged in a *fcc* lattice. The F^- ions fill all the tetrahedral holes in the face centred cubic lattice of Ca^{2+} ions. The edge of the unit cell is 5.46×10^{-8} cm in length. The density of the solid is 3.18 g cm^{-3}. Use this information to calculate Avogadro's number (Molar mass of CaF_2 = 78.08 g mol^{-1}).

(*A.I.S.B. 2010, D.S.B. 2010*)

14. The density of copper metal is 8.95 g cm^{-3}. If the radius of copper atom be 127.8 pm, is the copper unit cell simple cubic, body-centred cubic or face-centred cubic ?

(Given : atomic mass of Cu = 63.54 g mol^{-1} and $N_A = 6.022 \times 10^{23}$ mol^{-1}) (*A.I.S.B. 2010, D.S.B. 2010*)

15. Copper crystallises with face centred cubic unit cell. If the radius of copper atom is 127.8 pm, calculate the density of copper metal. (Atomic mass of Cu = 63.55 u and Avogadro's number $N_A = 6.02 \times 10^{23}$ mol^{-1})

(*A.I.S.B. 2012*)

16. Aluminium crystallizes in an *fcc* structure. Atomic radius of the metal is 125 pm. What is length of the side of the unit cell of metal ? (*A.I.S.B. 2013*)

[**Ans.** 353.3 pm]

17. An element with density 10 g cm^{-3} forms a cubic unit cell with edge length of 3×10^{-8} cm. What is the nature of the cubic unit cell if the atomic mass of the element is 81 g mol^{-1} ? (*A.I.S.B. 2015*)

[**Ans.** *bcc*]

18. An element crystallizes in *fcc* lattice with cell edge of 400 pm. The density of the element in 7 g cm^{-3}. How many atoms are present in 280 g of the element ? (*A.I.S.B. 2016*)

Hints & Answers for Revision Exercises

Very Short Answer Questions

2. 1

3. (*i*) 2N (*ii*) N

5. 12, 12

6. Schottky and Frenkel defects

9. 0.225 – 0.414

11. Electrical conductance increases.

13. Metal excess defect due to anion vacancies.

15. Conductivity of a semi-conductor increases with temperature.

17. P

18. Conductivity of metals decreases with increase in temperature.

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19. $a = 2\sqrt{2}\,r$ **22.** 1 mol
24. (*i*) 4 (*ii*) 2 **25.** (*i*) *p*-type (*ii*) *n*-type
26. 4 **27.** Frenkel defect
28. ferromagnetic **29.** X_2Y_3
30. $Na^+ = 6$, $Cl^- = 6$ **32.** six
33. Schottky defect **34.** *n*-type
35. Dipole-dipole forces **36.** Interstitial defect
38. X_4Y_3

Numerical Problems

• **1.** $\text{Density} = \dfrac{Z \times M}{a^3 \times N_A}$

$M = 39 + 127 = 166$

Z = No. of formula units

$$\therefore \quad 3.12 = \frac{Z \times 166}{(705 \times 10^{-10})^3 \times (6.022 \times 10^{23})}$$

$$Z = \frac{3.12 \times (705 \times 10^{-10})^3 \times (6.022 \times 10^{23})}{166}$$

$= 3.96$ or 4

$\therefore$ **4 K^+ and 4 I^-** ions per unit cell.

• **2.** $\text{Density} = \dfrac{Z \times M}{a^3 \times N_A}$

$$10.3 = \frac{Z \times 96}{(314 \times 10^{-10}\,\text{cm})^3 \times (6.022 \times 10^{23})}$$

$$Z = \frac{10.3 \times (314 \times 10^{-10})^3 \times 6.022 \times 10^{23}}{96} = \mathbf{2.0}$$

$\therefore$ *bcc* structure

• **3.** $$d(\text{NaCl}) = \frac{\frac{M(KCl)}{N_A}}{\frac{a^3(KCl)}{M(KCl)}} \times 4$$

$$d(\text{KCl}) = \frac{N_A}{a^3(KCl)} \times 4$$

$$\frac{d(\text{NaCl})}{d(\text{KCl})} = \frac{M(\text{NaCl})}{M(\text{KCl})} \times \left[\frac{a\,(\text{KCl})}{a\,(\text{NaCl})}\right]^3$$

$$= \frac{58.5}{74.5} \times \left(\frac{1}{0.875}\right)^3 = \mathbf{1.172}$$

• **4.** $\text{Density} = \dfrac{Z \times M}{a^3 \times N_A}$

For *bcc*, $Z = 2$

$$0.53 = \frac{2 \times 6.94}{a^3 \times 6.022 \times 10^{23}}$$

$$a^3 = \frac{2 \times 6.94}{0.53 \times 6.022 \times 10^{23}} = 4.35 \times 10^{-23}\ \text{cm}^3$$

Volume $= a^3 =$ **4.35×10^{-23} cm^3**

• **5.** For *bcc* arrangement, $Z = 2$, $\rho = 7.87\ \text{g cm}^{-3}$, $M = 56\ \text{g mol}^{-1}$

Edge length, $a = 286.65 \times 10^{-12}\ \text{m} = 286.65 \times 10^{-10}\ \text{cm}$

$$\rho = \frac{Z \times M}{a^3 \times N_A}$$

or $$N_A = \frac{Z \times M}{\rho^3 \times a^3}$$

$$= \frac{2 \times (56\ \text{g mol}^{-1})}{(7.87\ \text{g cm}^{-3}) \times (286.65 \times 10^{-10}\ \text{cm})^3}$$

$= \mathbf{6.04 \times 10^{23}\ mol^{-1}}$.

• **6.** Mass of unit cell $= \dfrac{180}{3.708 \times 10^{24}} \times 4 = 194.17 \times 10^{-24}$

$$\text{Density} = \frac{194.17 \times 10^{-24}}{(300 \times 10^{-10})^3} = 7.19\ \text{g cm}^{-3}$$

• **7.** Volume of unit cell $= (2.88 \times 10^{-8}\ \text{cm})^3$

$= 23.89 \times 10^{-24}\ \text{cm}^3$.

Volume of 156 g of element $= \dfrac{156\ \text{g}}{7.2\ \text{g cm}^{-3}} = 21.67\ \text{cm}^3$

No. of unit cells in this volume $= \dfrac{21.67}{23.89 \times 10^{-24}}$

$= 0.907 \times 10^{24}$

For *bcc*, number of atoms per unit cell = 2

$\therefore$ No. of atoms in 156 g of element $= 0.907 \times 10^{24} \times 2$

$= \mathbf{1.814 \times 10^{24}}$

• **8.** *Refer Solved Example 31 (page 39).*

• **9.** *Refer Solution of Practice Problem 38 (page 60).*

• **10.** *Refer Solution of Practice Problem 29 (page 59).*

• **11.** For fcc unit cell, radius , $r = \dfrac{a}{2\sqrt{2}}$

$$= \frac{409}{2 \times 1.414}$$

$= \mathbf{144.6pm}$

• **12.** 1 mol of tungsten = 184 g = 6.022×10^{23} atoms

No. of atoms in 1.5 g of tungsten $= \dfrac{6.023 \times 10^{23}}{184} \times 1.5$

A body centred cubic cell contains 2 atoms.

$$\text{No. of unit cells present} = \frac{6.023 \times 10^{23} \times 1.5}{184 \times 2}$$

$= \mathbf{2.45 \times 10^{21}}$

• **13.** $\text{Density} = \dfrac{Z \times M}{a^3 \times N_A}$

$$3.18\ \text{g cm}^{-3} = \frac{4 \times 78.08\ \text{g mol}^{-1}}{(5.46 \times 10^{-8}\,\text{cm})^3 \times N_A}$$

$\therefore \quad N_A =$ **6.02×10^{23}**

• **14.** Assuming *fcc* lattice for copper,

$a = 2\sqrt{2}\,r$

$= 2 \times 1.414 \times 127.8 \times 10^{-8}\ \text{cm}$

$= 3.614 \times 10^{-8}\ \text{cm}$

$$\text{Density, } \rho = \frac{4 \times 63.54}{(3.614 \times 10^{-8}\,\text{cm})^3 \times (6.02 \times 10^{23})}$$

$\therefore \quad = 8.94\ \text{g cm}^{-3}$

Since the density is same as observed, the lattice is ***fcc*** lattice.

• **15.** *Refer Solved Example 15 (page 35).*

• **16.** *Refer Solved Example 7 (page 17).*

• **17.** *Refer Solution of Practice Problem 32 (page 59).*

• **18.** *Refer Solution of Practice Problem 24 (page 58).*

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Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

X-RAYS DIFFRACTION STUDIES

X-rays studies have helped to know the arrangement of atoms, ions or molecules in crystals. The phenomenon of X-rays by the crystals was studied by W.L. Bragg and W.H. Bragg. By analysing the diffraction patterns, Bragg deduced a simple relationship between the distance between the planes of constituent particles in the crystal (d), the wavelength of X-rays used (λ) and the angle of diffraction (θ). This relation is known as Bragg equation and is given as:

$$n\lambda = 2d \sin \theta,$$

where 2θ = angle made by a diffracted X-ray beam with the direction of incident beam.

n = positive integer (1, 2, 3.... etc,) which stands for serial order of diffracted beams.

Using Bragg's law, we can calculate the distance between rows of constituent particles in a crystal. These distances are characteristic of a crystal and depend upon the size and geometry or arrangement of these particles.

LAW OF CONSTANCY OF INTERFACIAL ANGLES

Crystals are bound by plane faces. The angle between any two faces is called an **interfacial angle.** It is measured by an instrument known as **goniometer.** The **law of constancy of interfacial angles** states that

irrespective of the size and shape of the crystals (which depend upon the conditions of their formation), the angles between any two corresponding faces of the crystal of a particular substance are always the same.

This is also known as **Steno's law.**

STRUCTURE OF METALS

The crystal structures adopted by some metallic elements at 25°C and 1 bar pressure are :

Crystal structure	Elements
hcp	Be, Cd, Co, Mg, Ca, Ti, Zn
fcc	Ag, Al, Au, Ca, Cu, Ni, Pb, Pt
bcc	Ba, Cr, Fe, Ir, Alkali metals
Primitive cubic	Po

PACKING IN OXIDES OF IRON

The packing in oxides of iron such as FeO and Fe_3O_4 is very interesting.

Structure of Iron oxide (FeO)

Iron oxide (FeO) has rock salt (NaCl) structure. In this case O^{2-} ions adopt face centred cubic arrangement (*fcc*) and Fe^{2+} ions occupy octahedral sites. This is the ideal arrangement. However, this oxide is always non-stoichiometic *i.e.,* the composition of Fe^{2+} and O^{2-} ions is not 1 : 1. It has been found to be generally $Fe_{0.95}O$ (wustite). This composition can be obtained if a small number of Fe^{3+} ions are replaced by two-third as many Fe^{2+} ions in octahedral sites.

Structure of Magnetite (Fe_3O_4)

Magnetite may be considered as having the composition $FeO.Fe_2O_3$. This composition can be obtained if we convert 2/3 of Fe^{2+} ions in FeO into Fe^{3+} ions (for every three Fe^{2+} ions two Fe^{3+} ions). In Fe_3O_4, the oxide ions are arranged in cubic close packing arrangement. Fe^{2+} ions occupy octahedral sites and the Fe^{3+} ions are equally distributed between octahedral and tetrahedral sites. This structure is known as **inverse spinel structure**. Fe_3O_4 is the load stone used by ancient travellers to find the direction. Another example of this structure is $MgFe_2O_4$ in which Fe^{2+} ions of Fe_3O_4 are replaced by Mg^{2+} ions.

Normal Spinel Structure

A spinel is an important class of oxides consisting of two types of metal ions with the oxide ions. The general formula of the compounds adopting spinel structure is AB_2O_4 such as $MgAl_2O_4$ and ferrites such as $Zn\ Fe_2O_4$. In this case, the oxide ions are arranged in cubic close packing arrangement, the divalent cations (Mg^{2+} or Fe^{2+}) are in tetrahedral sites and trivalent ions (Fe^{3+}, Al^{3+}) are in octahedral sites. In normal spinel structure, one-eighth of the tetrahedral holes are occupied by divalent metal ions and one-half of the octahedral holes are occupied by trivalent metal ions. Many of the ferrites which have spinel type structures are important magnetic materials used in telephones or memory loops in computers.

DIELECTRIC PROPERTIES OF SOLIDS

Depending upon the alignment of dipoles, the crystals have the following dielectric properties:

(*a*) **Piezoelectricity** in which the dipoles align themselves in an ordered manner such that there is a net dipole moment in the crystal, *e.g.,* titanates of barium and lead, lead zirconate ($PbZrO_3$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), quartz.

(*b*) **Ferroelectricity** in which the dipoles are permanently aligned up even in the absence of electric field and the direction of polarization can be changed by applying an electric field. *e.g.,* barium titanate ($BaTiO_3$), sodium potassium tartarate (Rochelle salt), potassium dihydrogen phosphate (KH_2PO_4), etc.

(*c*) **Pyroelectricity.** Some polar crystals when heated produce small electric current called **pyroelectricity**.

(*d*) **Anti-ferroelectricity.** There is no net dipole moment in some crystals inspite of small dipoles because of alignment of dipoles in opposite directions and therefore they donot show ferroelectric character, *e.g.,* lead zirconate ($PbZrO_3$).

SUPERCONDUCTING MATERIALS

Ordinary metals conduct electricity and their conductivity is of order of $10^5\ ohm^{-1}\ m^{-1}$. **Superconducting materials** are those which offer no resistance to the passage of electricity. In this state, the materials become diamagnetic and are repelled by the magnets. Most metals become superconducting at very low temperatures (2–5 K). The highest temperature at which superconductivity was known till recently was 23 K in alloys of niobium (*e.g.,* Nb_3Ge). Some organic compounds also become superconducting at temperatures below 5 K.

The common examples of some superconducting materials along with their temperatures at which they become superconducting are given below :

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Material	Temperature
Alloys of niobium	23 K
$Ba_{0.7}K_{0.3}BiO_3$	30 K
$La_{1.8}Sr_{0.2}CuO_4$	40 K
$Bi_2Ca_2Sr_2Cu_3O_{10}$	105 K
$Tl_2Ca_2Ba_2Cu_3O_{10}$	125 K

The important possible uses of super conducting materials are in electronics, building magnets, levitation, transportation, power transmission, etc.

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions *M. C. Q.*

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Select the Correct Answer :

Space Lattice, Unit Cell and Crystal Systems

A1. The crystal system of a compound with unit cell dimensions, $a = 0.387$, $b = 0.387$ and $c = 0.504$ nm and $\alpha = \beta = 90°$ and $\gamma = 120°$ is
(a) cubic (b) hexagonal
(c) orthorhombic (d) rhombohedral

A2. In which of the following pair, both the crystals are not of the same type
(a) Ice, solid CO_2 (b) NaCl, BaO
(c) SiC, diamond (d) Mg, Ar

A3. Which of the following statements is not true about crystalline solids?
(a) Polar molecular solids have higher enthalpies of vaporisation than those of non-polar molecular solids.
(b) Graphite, though covalent solid is a good conductor of electricity.
(c) Ionic solids are conductors in molten state.
(d) Non-polar molecular solids have London forces between the constituents and have higher melting points than polar molecular solids.

A4. The most unsymmetrical and symmetrical systems are respectively
(a) tetragonal, cubic
(b) triclinic, cubic
(c) rhombohedral, hexagonal
(d) orthorhombic, cubic

A5. The packing fraction for a body centred cube is
(a) 0.42 (b) 0.54 (c) 0.68 (d) 0.74

A6. The number of atoms in *bcc* and *fcc* arrangement are respectively :
(a) 1, 2 (b) 2, 4 (c) 4, 2 (d) 2, 1

A7. The co-ordination number in *ccp* and *hcp* arrangement of metal atoms are respectively
(a) 6, 6 (b) 12, 6
(c) 8, 6 (d) 12, 12

A8. A metal crystallizes in a *ccp* structure. Its metallic radius is 141.5 pm. The number of unit cells in 64 cm^3 of the metal are
(a) 2×10^{32} (b) 1.5×10^{23}
(c) 1×10^{24} (d) 1.5×10^{22}

A9. The portion of edge length not occupied by atoms for simple cubic, *fcc* and *bcc* are respectively (a is edge length)
(a) $0 ; a\left(1-\frac{\sqrt{3}}{2}\right) ; a\left(1-\frac{1}{\sqrt{2}}\right)$
(b) $a\left(1-\frac{\sqrt{3}}{2}\right) ; 0 ; a\left(2-\frac{1}{\sqrt{2}}\right)$
(c) $0 ; a\left(1-\frac{1}{\sqrt{2}}\right) ; a\left(1-\frac{\sqrt{3}}{2}\right)$
(d) $a ; 2\sqrt{2}\,a ; \frac{\sqrt{3}}{2}a$

A10. Total volume of atoms present in face centred cubic unit cell of metal is (r is atomic radius)
(a) $\frac{24}{3}\pi r^3$ (b) $\frac{12}{3}\pi r^3$
(c) $\frac{16}{3}\pi r^3$ (d) $\frac{20}{3}\pi r^3$

A11. In a face centred cubic unit cell of close packed atoms, the radius of atom (r) is related to the edge length (a) of the unit cell by the expression
(a) $r = \frac{a}{\sqrt{2}}$ (b) $r = \frac{a}{2}$
(c) $r = \frac{a}{2\sqrt{2}}$ (d) $r = \frac{\sqrt{3}a}{4}$

A12. The number of atoms present in a hexagonal close packed unit cell is
(a) 4 (b) 6 (c) 8 (d) 12

Answers

A1. (b) **A2.** (d) **A3.** (d) **A4.** (b) **A5.** (c) **A6.** (b) **A7.** (d) **A8.** (c) **A9.** (c) **A10.** (c) **A11.** (c) **A12.** (b)

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A13. In a *hcp* arrangement, each atom at the corner contributes to the unit cell equal to
(*a*) 1/2 (*b*) 1/8 (*c*) 1/6 (*d*) 1/4

A14. A metal crystallizes in *bcc* lattice. The percentage of edge length not covered by atoms is
(*a*) 12.4% (*b*) 13.4%
(*c*) 87.6% (*d*) 50.0%

A15. A metal crystallizes in *fcc* lattice and edge of the unit cell is 620 pm. The radius of metal atom is
(*a*) 265.5 pm (*b*) 310 pm
(*c*) 219.2 pm (*d*) 438.6 pm

A16. How many unit cells are present in a cubic shaped ideal crystal of NaCl of mass 1.0 g ?
(*a*) 2.57×10^{21} (*b*) 1.28×10^{21}
(*c*) 1.71×10^{21} (*d*) 5.14×10^{21}

Interstitial Voids, Structure and Density of Ionic solids

A17. For tetrahedral co-ordination, the radius ratio (r_+/r_-) should be :
(*a*) 0.155 – 0.225 (*b*) 0.225 – 0.414
(*c*) 0.414 – 0.732 (*d*) 0.732 – 1

A18. A compound formed by elements A and B crystallises in the cubic structure where A atoms are at the corners of a cube and B atoms are at the face centre. The formula of the compound is :
(*a*) AB_3 (*b*) A_2B (*c*) AB_2 (*d*) A_2B_3.

A19. The number of second nearest Na^+ ions neighbour of a Na^+ ion in NaCl structure is
(*a*) 12 (*b*) 6 (*c*) 8 (*d*) 4

A20. The cubic unit cell of Al (molar mass = 27 g mol^{-1}) has an edge length of 405 pm. Its density is 2.7 g cm^{-3}. The cubic unit cell is
(*a*) body centred (*b*) primitive
(*c*) edge centred (*d*) face centred

A21. In magnetite, O^{2-} have *ccp* arrangement with Fe^{2+} ions in 1/8th tetrahedral voids and Fe^{3+} ions in 1/4th octahedral and 1/8th tetrahedral voids. The formula of magnetite is
(*a*) Fe_3O_4 (*b*) Fe_2O_3
(*c*) FeO (*d*) Fe_3O_8

A22. An alloy of Cu, Au and Ag is found to have Cu constituting the *ccp* lattice. If Ag atoms occupy edge centres and Au is present at body centres, the alloy has formula :
(*a*) $Cu_4\ Ag_2\ Au$ (*b*) $Cu_4\ Ag_4\ Au$
(*c*) $Cu_4\ Ag_3\ Au$ (*d*) Cu Ag Au

A23. In spinel structure, O^{2-} ions are cubic-closed packed, whereas 1/8th of the tetrahedral holes are occupied by A^{2+} cations and 1/2 of the octahedral holes are occupied by cations B^{3+}. The general formula of this compound is
(*a*) A_2BO_4 (*b*) AB_2O_4
(*c*) A_2B_4O (*d*) A_4B_2O

A24. A crystalline solid has a cubic structure in which tungsten (W) atoms are located at the cubic corners of the unit cell, oxygen atoms at the edges of the cube and sodium atoms at the cube centre. The molecular formula of the compound is
(*a*) Na_2WO_3 (*b*) $NaWO_4$
(*c*) $NaWO_3$ (*d*) Na_2WO_4

A25. A mineral of titanium (perovskite) is found to contain calcium ions at the corners, oxygen atoms at the face centres and titanium atoms at the centre of the cube. The oxidation state of titanium in the mineral is
(*a*) + 1 (*b*) + 3 (*c*) + 4 (*d*) + 2

A26. The number of tetrahedral and octahedral holes in a hexagonal primitive unit cell are
(*a*) 8, 4 (*b*) 6, 12 (*c*) 2, 1 (*d*) 12, 6

A27. In which of the following structures, the anion has maximum co-ordination number ?
(*a*) NaCl (*b*) ZnS (*c*) CaF_2 (*d*) Na_2O

A28. In a *fcc* arrangement of P and Q atoms, where P atoms are at the corners of the unit cell, Q atoms at the face centres and two atoms are missing from two corners in each unit cell, then the formula of the compound is
(*a*) P_2Q_3 (*b*) P_4Q (*c*) P_4Q_5 (*d*) PQ_4

A29. The pyknometer density of sodium chloride crystal is 2.165×10^3 kg m^{-3} while its X-ray density is 2.178×10^3 kg m^{-3}. The fraction of the unoccupied sites in sodium chloride crystal is
(*a*) 5.96 (*b*) 5.96×10^{-2}
(*c*) 5.96×10^{-1} (*d*) 5.96×10^{-3}

A30. Three elements A, B and C crystallise into a cubic solid lattice. Atoms A occupy the corners, B occupy the cube centres and C occupy the edges. The formula of the compound is
(*a*) ABC (*b*) ABC_2
(*c*) ABC_3 (*d*) ABC_4

A31. A element cystallizes in *fcc* lattice and edge length of unit cell is 400 pm. If density of unit cell is 11.2 g cm^{-3}, then atomic mass of the element is
(*a*) 215.6 (*b*) 431.2
(*c*) 107.8 (*d*) 98.6

A32. An element (atomic mass = 60 g mol^{-1}) having fcc unit cell has density 6.23 g cm^{-3}. The edge length of the unit cell is ($N_A = 6.02 \times 10^{23}$)
(*a*) 300 pm (*b*) 250 pm
(*c*) 400 pm (*d*) 160 pm

Answers

A13. (*c*) **A14.** (*b*) **A15.** (*c*) **A16.** (*a*) **A17.** (*b*) **A18.** (*a*) **A19.** (*a*) **A20.** (*d*) **A21.** (*a*) **A22.** (*c*)
A23. (*b*) **A24.** (*c*) **A25.** (*c*) **A26.** (*d*) **A27.** (*d*) **A28.** (*d*) **A29.** (*d*) **A30.** (*c*) **A31.** (*c*) **A32.** (*c*)

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A33. The cell edge of a fcc crystal is 100 pm and its density is 10.0 g cm^{-3}. The number of atoms in 100 g of this crystal is
(a) 1×10^{25} (b) 2×10^{25}
(c) 3×10^{25} (d) 4×10^{25}

A34. Copper crystallizes in a cubic lattice structure. Atomic radius of copper is 128 pm and its atomic mass is 63.5. The density of copper is
(a) 10.71 g cm^{-3} (b) 4.93 g cm^{-3}
(c) 8.9 g cm^{-3} (d) 11.2 g cm^{-3}

Defects in Crystal Structures, Magnetic and Electrical Properties

A35. Which of the following is not an example of 13–15 compound?
(a) InSb (b) GaAs
(c) CdSe (d) AlP.

A36. If the alignment of magnetic moments in a substance is in a compensatory way so as to give zero net magnetic moment, then the substance is said to be
(a) ferromagnetism (b) anti-ferromagnetism
(c) ferrimagnetism (d) diamagnetism.

A37. Fe_3O_4 is ferrimagnetic at room temperature but at 850 K it becomes :
(a) diamagnetic (b) ferromagnetic
(c) non-magnetic (d) paramagnetic

A38. Iron (II) oxide has cubic structure and each unit cell has side 5Å. If the density of the compound is 4 g cm^{-3}, calculate the number of Fe^{2+} and O^{2-} ions present in each unit cell. (molar mass of FeO = 72 g mol^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1})
(a) 1 (b) 2
(c) 4 (d) 6

A39. The appearance of colour in solid alkali metal halides is generally due to
(a) Schottky defect (b) Frenkel defect
(c) Interstitial position (d) F-centres
(C.B.S.E PMT. 2006)

A40. An example of a ferromagnetic oxide is
(a) CrO_2 (b) TiO_2
(c) Fe_3O_4 (d) Mn_2O_7

Answers

A33. (d) **A34.** (c) **A35.** (c) **A36.** (b) **A37.** (d) **A38.** (c) **A39.** (d) **A40.** (a)

B MULTIPLE CHOICE QUESTIONS *from Competitive Examinations*

AIPMT & Other State Boards' Medical Entrance

B1. If NaCl is doped with 10^{-4} mol % of $SrCl_2$, the concentra-tion of cation vacancies will be ($N_A = 6.02 \times 10^{23}$ mol^{-1})
(a) 6.02×10^{16} mol^{-1} (b) 6.02×10^{17} mol^{-1}
(c) 6.02×10^{14} mol^{-1} (d) 6.02×10^{15} mol^{-1}
(C.B.S.E. PMT. 2007)

B2. The fraction of total volume occupied by the atoms present in a simple cube is
(a) $\frac{\pi}{3\sqrt{2}}$ (b) $\frac{\pi}{4\sqrt{2}}$
(c) $\frac{\pi}{4}$ (d) $\frac{\pi}{6}$ *(C.B.S.E.P.M.T.2007)*

B3. If '*a*' stands for the edge length of the cubic systems: simple cubic, body centred cubic and face centred cubic, then the ratio of the radii of the spheres in these systems will be respectively :
(a) $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$ (b) $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$
(c) $\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{2}}{2}a$ (d) $1a : \sqrt{3}a : \sqrt{2}a$
(C.B.S.E. PMT 2008)

B4. Lithium metal crytallises in a body centred cubic crystal. If the length of the side of the unit cell of lithium is 351 pm, the atomic radius of the lithium will be :
(a) 151.8 pm (b) 75.5 pm
(c) 300.5 pm (d) 240.8 pm
(C.B.S.E. PMT 2009)

B5. A metal crystallises with a face-centred cubic lattice. The edge of the unit cell is 408 pm. The diameter of the metal atom is
(a) 288 pm (b) 408 pm
(c) 144 pm (d) 204 pm *(A.I.P.M.T. 2012)*

B6. A metal has a *fcc* lattice. The edge length of the unit cell is 404 pm. The density of the metal is 2.72 g cm^{-3}. The molar mass of the metal is:
(Avogadro's constant, $N_A = 6.02 \times 10^{23}$ mol^{-1})
(a) 27 g mol^{-1} (b) 20 g mol^{-1}
(c) 40 g mol^{-1} (d) 30 g mol^{-1} *(NEET 2013)*

B7. The number of carbon atoms per unit cell of diamond unit cell is
(a) 6 (b) 1
(c) 4 (d) 8 *(NEET 2013)*

Answers

B1. (b) **B2.** (d) **B3.** (a) **B4.** (a) **B5.** (a) **B6.** (a) **B7.** (d)

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B8. If a is the length of the side of a cube, the distance between the body centered atom and *one* corner atom in the cube will be

(a) $\frac{2}{\sqrt{3}}a$ (b) $\frac{4}{\sqrt{3}}a$

(c) $\frac{\sqrt{3}}{4}a$ (d) $\frac{\sqrt{3}}{2}a$ *(AIPMT 2014)*

B9. The vacant space in *bcc* lattice unit cell is :

(a) 23% (b) 32%

(c) 26% (d) 48% *(AIPMT 2015)*

B10. The correct statement regarding defects in crystalline solids is :

(a) Frenkel defect is a dislocation defect.

(b) Frenkel defect is found in halides of alkaline earth metals.

(c) Schottky defects have no effect on the density of crystalline solids.

(d) Frenkel defects decrease the density of crystalline solids. *(AIPMT 2015)*

B11. A given metal crystallises out with a cubic structure having edge length of 361 pm. If there are four metal atoms in one unit cell, what is the radius of one atom ?

(a) 80 pm (b) 108 pm

(c) 40 pm (d) 127 pm *(AIPMT 2015)*

B12. Lithium has a *bcc* structure. Its density is 530 kg m^{-3} and its atomic mass is 6.94 g mol^{-1}. Calculate the edge length of a unit cell of lithium metal. (N_A = 6.02×10^{23} mol^{-1})

(a) 527 pm (b) 264 pm

(c) 154 pm (d) 352 pm *(NEET 2016)*

B13. The ionic radii of A^+ and B^- ions are 0.98×10^{-10} m and 1.81×10^{-10} m. The coordination number of each ion in AB is

(a) 8 (b) 2

(c) 6 (d) 4 *(NEET 2016)*

B14. In calcium fluoride, having the fluorite structure, the coordination numbers for calcium ion (Ca^{2+}) and fluoride ion (F^-) are

(a) 4 and 2 (b) 6 and 6

(c) 8 and 4 (d) 4 and 8 *(NEET 2016)*

B15. Which is the incorrect statement ?

(a) Density decreases in case of crystals with Schottky defect.

(b) NaCl(*s*) is insulator, silicon is semiconductor, silver is conductor, quartz is piezoelectric crystal.

(c) Frenkel defect is favoured in those ionic compounds in which sizes of cations and anions are almost equal.

(d) $FeO_{0.98}$ has non-stoichiometric metal deficiency defect. *(NEET 2017)*

B16. Iron exhibits bcc structure at room temperature. Above 900 °C, it transforms to fcc structure. The ratio of density of iron at room temperature to that at 900 °C (assuming molar mass and atomic radii of iron remain constant with temperature) is

(a) $\frac{\sqrt{3}}{\sqrt{2}}$ (b) $\frac{4\sqrt{3}}{3\sqrt{2}}$

(c) $\frac{3\sqrt{3}}{4\sqrt{2}}$ (d) $\frac{1}{2}$ *(NEET 2018)*

B17. Total number of tetrahedral and octahedral voids in 0.5 mol of a compound forming *hcp* structure are :

(a) 6.022×10^{23} (b) 3.011×10^{23}

(c) 9.033×10^{23} (d) 4.516×10^{23}

(A.M.U Med. 2010)

B18. Which one of the following compound exhibits both Schottky and Frenkel defects ?

(a) NaCl (b) AgCl

(c) AgBr (d) AgI

(A.M.U. Med. 2010)

B19. The mass percentage of iron present as Fe(III) in $Fe_{0.93}O_{1.0}$ is

(a) 8.3% (b) 9.6%

(c) 11.5% (d) 17.7% *(A.M.U. Med. 2013)*

JEE (Main) & Other State Boards' Engineering Entrance

B20. In a compound, atoms of element Y form ccp lattice and those of element X occupy 2/3rd of tetrahedral voids. The formula of the compound will be

(a) X_3Y_4 (b) X_4Y_3

(c) X_2Y_3 (d) X_2Y *(A.I.E.E.E. 2008)*

B21. The edge length of a face centred cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is :

(a) 618 pm (b) 144 pm

(c) 288 pm (d) 398 pm

(A.I.E.E.E. 2010)

B22. Percentage of free space in cubic close packed structure and in body centred packed structure are respectively :

(a) 32 % and 48 % (b) 48 % and 26%

(c) 30 % and 26 % (d) 26% and 32%

(A.I.E.E.E. 2010)

Answers

B8. (d) **B9.** (b) **B10.** (a) **B11.** (d) **B12.** (d) **B13.** (c) **B14.** (c) **B15.** (c,d) **B16.** (c) **B17.** (c)
B18. (c) **B19.** (c) **B20.** (b) **B21.** (b) **B22.** (d)

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B23. In a face centred cubic lattice, atom A occupies the corner positions and atom B occupies the face centre positions. If one atom of B is missing from one of the face centred points, the formula of the compound is

(a) A_2B (b) AB_2

(c) A_2B_3 (d) A_2B_5 (*AIEEE 2011*)

B24. Copper crystallises in *fcc* lattice with a unit cell edge of 361 pm. The radius of copper atom is :

(a) 108 pm (b) 128 pm

(c) 157 pm (d) 181 pm (*AIEEE 2011*)

B25. Lithium forms body centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be

(a) 300 pm (b) 240 pm

(c) 152 pm (d) 75 pm (*A.I.E.E.E. 2012*)

B26. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M is present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be

(a) 5.08% (b) 7.01%

(c) 4.08% (d) 6.05%

(*JEE Main 2013*)

B27. CsCl crystallises in body-centred cubic lattice. If '*a*' is its edge length then which of the following expression is correct ?

(a) $r_{Cs^+} + r_{Cl^-} = \sqrt{3}\,a$ (b) $r_{Cs^+} + r_{Cl^-} = 3a$

(c) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$ (d) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$

(*JEE Main 2014*)

B28. Sodium metal crystallizes in a body centred cubic lattice with a unit cell edge 4.29 Å. The radius of sodium atom is approximately

(a) 5.72 Å (b) 0.93 Å

(c) 1.86 Å (d) 3.22 Å (*JEE Main 2015*)

B29. Which of the following compound is metallic and ferromagnetic?

(a) TiO_2 (b) CrO_2

(c) VO_2 (d) MnO_2 (*JEE Main 2016*)

B30. A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is '*a*', the closest approach between two atoms in metallic crystal will be

(a) $2a$ (b) $2\sqrt{2}a$

(c) $\sqrt{2}a$ (d) $\frac{a}{\sqrt{2}}$ (*JEE Main 2017*)

B31. Which type of 'defect' has the presence of cations in the interstitial sites?

(a) Schottky defect (b) Vacancy defect

(c) Frenkel defect (d) Metal deficiency defect

(*JEE Main 2018*)

B32. An ionic compound is expected to have tetrahedral structure if r_+/r_- lies in the range of

(a) 0.155 to 0.225 (b) 0.732 to 1

(c) 0.414 to 0.732 (d) 0.225 to 0.414

(*Karnataka C.E.T. 2008*)

B33. A solid compound contains X, Y and Z atoms in a cubic lattice with X atoms occupying the corners, Y atoms in the body centred position and Z atoms at the centres of faces of the unit cell. What is the empirical formula of the compound?

(a) XY_2Z_3 (b) XYZ_3

(c) $X_2Y_2Z_3$ (d) X_8YZ_6

(e) XYZ (*Kerala P.E.T. 2008*)

B34. KCl crystallizes in the same type of lattice as does NaCl. Given that $r_{Na^+}/r_{Cl^-} = 0.55$ and $r_{K^+}/r_{Cl^-} = 0.74$, calculate the ratio of the side of the unit cell for KCl to that of NaCl.

(a) 1.123 (b) 0.891

(c) 1.414 (d) 0.414

(e) 1.732 (*Kerala P.E.T. 2008*)

B35. The white ZnO turns yellow on heating because of

(a) Frenkel defect

(b) Metal excess defect

(c) Metal deficiency defect

(d) Schottky defect (*A.M.U. Engg. 2010*)

B36. In face-centred cubic lattice, a unit cell is shared equally by how many unit cells?

(a) 6 (b) 4

(c) 2 (d) 8

(*Karnataka C.E.T. 2013*)

B37. Potassium dichromate belongs to which crystal system?

(a) Tetragonal (b) Orthorthombic

(c) Triclinic (d) Hexagonal

(e) Monoclinic (*Kerala PET 2014*)

B38. Which one of the following is used as a piezoelectric material ?

(a) Silicones (b) Graphite

(c) Silica gel (d) Kieselguhr

(e) Quartz

(*Kerala PET 2014, Karnataka CET 2016*)

Answers

B23. (d) **B24.** (b) **B25.** (c) **B26.** (c) **B27.** (d) **B28.** (c) **B29.** (b) **B30.** (d) **B31.** (c) **B32.** (d)
B33. (b) **B34.** (a) **B35.** (b) **B36.** (a) **B37.** (c) **B38.** (e)

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B39. Suppose the mass of a single Ag atom is '*m*'. Ag metal crystallizes in *fcc* lattice with unit cell of length '*a*'. The density of Ag metal in terms of '*a*' and '*m*' is

(*a*) $\frac{4m}{a^3}$ (*b*) $\frac{2m}{a^3}$

(*c*) $\frac{m}{a^3}$ (*d*) $\frac{m}{4a^3}$

(*WB JEE 2015*)

B40. The unit cell with crystallographic dimensions, $a \neq b \neq c$, $\alpha = \gamma = 90°$ and $\beta \neq 90°$ is

(*a*) monoclinic (*b*) tetragonal

(*c*) triclinic (*d*) orthorhombic

(*Karnataka CET 2015*)

B41. Ionic solids with Schottky defect may contain in their structure

(*a*) cation vacancies only

(*b*) cation vacancies and interstitial cations

(*c*) equal number of cation and anion vacancies

(*d*) anion vacancies and interstitial anions

(*WB JEE 2016, Karnataka CET 2016*)

B42. In a face centred cubic unit cell, what is the volume occupied?

(*a*) $\frac{4}{3}\pi r^3$ (*b*) $\frac{8}{3}\pi r^3$

(*c*) $\frac{16}{3}\pi r^3$ (*d*) $\frac{64r^3}{3\sqrt{3}}$

(*MH CET 2016*)

B43. An element crystallising in body centred cubic lattice has an edge length of 500 pm. If its density is 4 g cm^{-3}, the atomic mass of the element (in g mol^{-1}) is (consider $N_A = 6 \times 10^{23}$)

(*a*) 100 (*b*) 250

(*c*) 125 (*d*) 150

(*e*) 50 (*Kerala PET 2016*)

B44. The contribution of a particle at the edge centre of a particular unit cell is,

(*a*) $\frac{1}{2}$ (*b*) $\frac{1}{4}$

(*c*) 1 (*d*) $\frac{1}{8}$

(*Karnataka CET 2016*)

B45. The correct statement regarding defect in solids is

(*a*) Schottky defect has no effect on the physical properties of solids

(*b*) Frenkel defect is a dislocation defect

(*c*) Frenkel defect is usually favoured by a very small difference in the sizes of cations and anions

(*d*) Trapping of proton in the lattice leads to the formation of F-centres. (*Karnataka CET 2017*)

B46. Which of the following crystals has unit cell such that $a \neq b \neq c$ and $\alpha \neq \beta \neq \Upsilon \neq 90°$?

(*a*) $K_2Cr_2O_7$ (*b*) $NaNO_3$

(*c*) KNO_3 (*d*) A_8B_7

(*Karnataka CET 2017*)

B47. In a face centred cubic arrangement of A and B atoms in which 'A' atoms are at the corners of the unit cell and 'B' atoms are at the face centres. One of the 'A' atoms is missing from one corner in unit cell. The simplest formula of compound is

(*a*) AB_3 (*b*) A_7B_{24}

(*c*) A_7B_8 (*d*) A_7B_3

(*Karnataka CET 2017*)

B48. A compound formed by elements X and Y crystallises in the cubic structure, where X atoms at the corners of a cube and Y atoms are at the centres of the body. The formula of the compound is

(*a*) XY (*b*) XY_2

(*c*) X_2Y_3 (*d*) XY_3 (*WB JEE 2018*)

B49. Edge length of a cube is 300 pm. Its body diagonal would be

(*a*) 600 pm (*b*) 423 pm

(*c*) 519.6 pm (*d*) 450.5 pm

(*Karnataka CET 2018*)

B50. Which of the following is not a conductor of electricity?

(*a*) Solid NaCl (*b*) Cu

(*c*) Fused NaCl (*d*) Brine solution

(*Karnataka CET 2018*)

JEE (Advance) for IIT Entrance

B51. In a solid 'AB' having NaCl structure, 'A' atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the resultant stiochiometry of the solid is

(*a*) AB_2 (*b*) A_2B

(*c*) A_4B_3 (*d*) A_3B_4 (*I.I.T. 2001*)

B52. In which of the following crystals alternate tetrahedral voids are occupied ?

(*a*) NaCl (*b*) ZnS

(*c*) CaF_2 (*d*) Na_2O (*I.I.T. 2005*)

Answers

B39. (*a*) **B40.** (*a*) **B41.** (*c*) **B42.** (*c*) **B43.** (*d*) **B44.** (*b*) **B45.** (*b*) **B46.** (*a*) **B47.** (*b*) **B48.** (*a*)
B49. (*c*) **B50.** (*a*) **B51.** (*d*) **B52.** (*b*)

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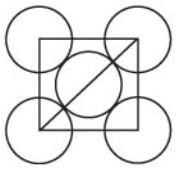
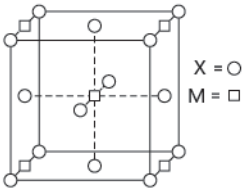
B53. The packing efficiency of the two dimensional square unit cell shown is :



(*a*) 39.27 % (*b*) 68.02%
(*c*) 74.05% (*d*) 78.54% (*I.I.T. 2010*)

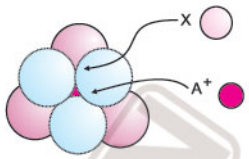
B54. A compound M_pX_q has cubic close packing (*ccp*) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is



(*a*) MX (*b*) MX_2
(*c*) M_2X (*d*) M_5X_{14}

(*I.I.T. J.E.E. 2012*)

B55. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is



(*a*) 104 pm (*b*) 125 pm
(*c*) 183 pm (*d*) 57 pm

(*JEE Advance 2013*)

B56. If the unit cell of a mineral has cubic close packed (*ccp*) array of oxygen atoms with *m* fraction of octahedral holes occupied by aluminium ions and *n* fraction of tetrahedral holes occupied by magnesium ions, *m* and *n*, respectively, are

(*a*) $\frac{1}{2}, \frac{1}{8}$ (*b*) $1, \frac{1}{4}$
(*c*) $\frac{1}{2}, \frac{1}{2}$ (*d*) $\frac{1}{4}, \frac{1}{8}$

(*JEE Advance 2015*)

Answers

B53. (*d*) **B54.** (*b*) **B55.** (*a*) **B56.** (*a*)

C MULTIPLE CHOICE QUESTIONS
with more than one correct answer

C1. Which of the following is/are not true about hexagonal close packing ?
(*a*) It has 26% empty space
(*b*) In this arrangement, third layer is identical to the first layer.
(*c*) The coordination number in this arrangement is 6.
(*d*) It is as closely packed as body centred cubic packing.

C2. Which of the following statements are correct ?
(*a*) The coordination number of each type of ion in CsCl crystal is 8.
(*b*) A metal that crystallizes in bcc structure has coordination number 12.
(*c*) A unit cell of an ionic crystal shares some of its ions with other unit cells.
(*d*) The length of the unit cell in NaCl is 552 pm (r_{Na^+} = 95 pm, r_{Cl^-} = 181 pm)

C3. In which of the following structures, the coordination number of both the ions are same ?
(*a*) Cesium chloride
(*b*) Sodium chloride
(*c*) Zinc sulphide
(*d*) Sodium oxide

C4. Which of the following is not correct for Frenkel defect in crystals ?
(*a*) It is due to equal number of cations and anions missing from lattice sites.
(*b*) It has no effect on density of the crystal.
(*c*) It occurs in crystals where the difference in the size of cations and anions is small.
(*d*) Silver halides show Frenkel defect.

C5. The coordination number of eight for cation is found in
(*a*) CsCl (*b*) NaCl
(*c*) CaF_2 (*d*) Na_2O

C6. Which of the following systems do not give correct description of axial lengths and axial angles ?
(*a*) Hexagonal : $a = b \neq c$, $\alpha = \beta = 90°, \gamma = 120°$
(*b*) Tetragonal : $a = b \neq c$, $\alpha = \beta = 90°, \gamma \neq 90°$

Answers

C1. (*c*), (*d*) **C2.** (*a*), (*c*), (*d*) **C3.** (*a*), (*b*), (*c*) **C4.** (*a*), (*c*) **C5.** (*a*), (*c*) **C6.** (*b*), (*c*)

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(c) Monoclinic : $a \neq b \neq c$, $\alpha = \beta = \gamma \neq 90°$

(d) Cubic : $a = b = c$, $\alpha = \beta = \gamma = 90°$

C7. The correct statement(s) regarding defects in solids is (are)

(a) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion

(b) Frenkel defect is a dislocation defect

(c) Trapping of an electron in the lattice leads to the formation of F-centre

(d) Schottky defects have no effect on the physical properties of solids. *(IIT-JEE 2009)*

C8. With respect to graphite and diamond, which of the statement(s) given is(are) correct ?

(a) Graphite is harder than diamond.

(b) Graphite has higher electrical conductivity than diamond.

(c) Graphite has higher thermal conductivity than diamond.

(d) Graphite has higher C—C bond order than diamond. *(IIT-JEE 2012)*

C9. Which type of defects are present in AgBr and ZnS crystal systems ?

(a) Frenkel and Schottky

(b) Schottky and Frenkel

(c) Frenkel and Frenkel

(d) Schottky and Schottky *(A.M.U. (Engg.) 2015)*

C10. The correct statement(s) for cubic close packed (*ccp*) in three dimensional structure is(are)

(a) the number of the nearest neighbours of an atom present in the top most layer is 12.

(b) the efficiency of atom packing is 74%.

(c) the number of octahedral and tetrahedral voids per atom are 1 and 2, respectively.

(d) the unit cell edge length is $2\sqrt{2}$ times the radius of the atom.

(JEE Advance 2016)

Answers

C7. (b), (c) **C8.** (b), (d) **C9.** (b), (c) **C10.** (b), (c), (d)

D MULTIPLE CHOICE QUESTIONS

based on the given passage/comprehension

Passage I.

In the crystalline solids the smallest repeating part in the lattice is known as unit cell. The unit cells are described as simple (points at all the corners), body centred (points at all the corners and in the centre), face centred (points at all the corners and centre of all faces), and end centred (points at all the corners and centres of two opposite end faces) unit cells. In two common types of packing *ccp* and *hcp*, 26% of space is left unoccupied in the form of interstitial sites. For the stable ionic crystalline structures, there is definite radius ratio limit for a cation to fit perfectly in the lattice of anions, called radius ratio rule. This also defines the coordination number of an ion, which is the number of nearest neighbours of opposite charges. This depends upon the ratio of radii of two types of ions, r_+/r_-. This ratio for coordination numbers 3, 4, 6 and 8 is respectively 0.155–0.225, 0.225–0.414, 0.414–0.732 and 0.732–1 respetively.

Answer the following questions :

D1. The number of atoms per unit cell in simple (s), body centred (*b*), face centred (*f*) and end centred (*e*) unit cell decreases as

(a) $f > b > e > s$ (b) $f > b = e > s$

(c) $b > f > s = e$ (d) $f > b > e = s$

D2. Gold crystallizes in a face centred unit cell. Its edge length is 0.410 nm. The radius of gold atom is

(a) 0.205 nm (b) 0.290 nm

(c) 0.145 nm (d) 0.578 nm

D3. In a cubic lattice of XYZ, X atoms are present at all corners except one corner which is occupied by Y atoms. Z atoms are present at face centres. The formula of the compound is

(a) X_8YZ_{24} (b) XYZ_3

(c) $X_7Y_{24}Z$ (d) X_7YZ_{24}

D4. The ionic radii of K^+, Rb^+ and Br^- are 137, 148 and 195 pm. The coordination number of cation in RbBr and KBr structures are respectively

(a) 8, 6 (b) 6, 4

(c) 6, 8 (d) 4, 6

D5. A face centred cubic lattice of a metal M and a body centred cubic lattice of metal N contain same number of 2.25×10^{22} unit cells. If density of M is twice than that of N, the ratio between the number of atoms per unit cell is

(a) 4 : 1 (b) 1 : 1

(c) 2 : 1 (d) 1 : 4

Passage II.

Density of a unit cell is same as the density of the substance. If the density of the substance is known, number of atoms or dimensions of the unit cell can be calculated. The density of the unit cell is related to its mass (M), no. of atoms per unit cell (Z), edge length (*a* in cm) and Avogadro number N_A as :

$$\rho = \frac{Z \times M}{a^3 \times N_A}$$

Answers

Passage – I **D1.** (b) **D2.** (c) **D3.** (d) **D4.** (a) **D5.** (c)

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Answer the following questions :

D6. An element crystallizes in a structure having a fcc unit cell of an edge 100 pm. If 24 g of the element contains 24×10^{23} atoms, the density is

(*a*) 2.40 g cm^{-3} (*b*) 40 g cm^{-3}

(*c*) 4 g cm^{-3} (*d*) 24 g cm^{-3}

D7. The number of atoms present in 100 g of a *bcc* crystal (density = 12.5 g cm^{-3}) having cell edge 200 pm is

(*a*) 1×10^{25} (*b*) 1×10^{24}

(*c*) 2×10^{24} (*d*) 2×10^{26}

D8. A metal X (at. mass = 60) has a body centred cubic crystal structure. The density of the metal is 4.2 g cm^{-3}. The volume of unit cell is

(*a*) 8.2×10^{-23} cm^3 (*b*) 4.75×10^{-23} cm^3

(*c*) 3.86×10^{23} cm^3 (*d*) 3.86×10^{-23} cm^3

Passage III.

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism.

Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (*hcp*), is constituted of a sphere on a flat surface

surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of the three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be '*r*'.

Answer the following questions :

D9. The number of atoms in this *hcp* unit cell is

(*a*) 4 (*b*) 6 (*c*) 12 (*d*) 17

D10. The volume of this *hcp* unit cell is

(*a*) $24\sqrt{2}r^3$ (*b*) $16\sqrt{2}r^3$

(*c*) $12\sqrt{2}r^3$ (*d*) $\frac{64}{3\sqrt{3}}r^3$

D11. The empty space in this *hcp* unit cell is

(*a*) 74% (*b*) 47.6%

(*c*) 32% (*d*) 26% (*I.I.T. 2008*)

Answers

Passage–II **D6.** (*b*) **D7.** (*c*) **D8.** (*b*)

Passage–III **D9.** (*b*) **D10.** (*a*) **D11.** (*d*)

Assertion Reason Type Questions

The questions given below consist of an Assertion and the Reason. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reason is the correct explanation of the assertion.

(*b*) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.

(*c*) If assertion is CORRECT but reason is INCORRECT.

(*d*) If assertion is INCORRECT but reason is CORRECT.

(*e*) If both assertion and reason are INCORRECT.

1. Assertion : In any ionic solid (MX) with Schottky defects, the number of positive and negative ions are same.
Reason : Equal number of cation and anion vacancies are present. (*I.I.T. 2001*)

2. Assertion : ZnS has a tetrahedral arrangement.
Reason : In ZnS, S^{2-} ions occupy the tetrahedral sites while Zn^{2+} ions form cubic close packed structure.

3. Assertion : In CsCl structure, the co-ordination number of Cs^+ ion is 8.
Reason : Cl^- ions in CsCl have body centred cubic arrangement.

4. Assertion : In ZnO, the excess Zn^{2+} ions are present in interstitial sites.
Reason : Metal excess crystals have either missing cation or anion in interstitial site.

5. Assertion : FeO is non-stoichiometric with $Fe_{0.95}O$.
Reason : Some Fe^{2+} ions are replaced by Fe^{3+} as $3Fe^{2+} = 2Fe^{3+}$ to maintain electrical neutrality.

6. Assertion : In CaF_2, F^- ions occupy all the tetrahedral sites.
Reason : The number of Ca^{2+} is double the number of F^- ions.

7. Assertion : Size of cation is larger in tetrahedral void than in octahedral void.
Reason : The cations occupy more space than anions in crystal close packing

8. Assertion : Frenkel defect is shown by silver halides.
Reason : Silver ions are small in size and can easily fit in interstitial sites.

9. Assertion : In Frenkel defect, density of the crystalline solid does not change.
Reason : In Frenkel defect, no cation or anion leaves the crystal.

10. Assertion : Frenkel and Schottky defects are stoichiometric defects.
Reason : Both defects change the density of the crystalline solid.

Answers

(1) – (*a*) **(2)** – (*e*) **(3)** – (*c*) **(4)** – (*c*) **(5)** – (*a*) **(6)** – (*c*) **(7)** – (*e*) **(8)** – (*a*) **(9)** – (*a*) **(10)** – (*c*)

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Matching Type Questions

Each question has matching list. The codes for the lists have choices (*a*), (*b*), (*c*) and (*d*) out of which only one is correct.

1. Match the type of crystal system given in List I with its description given in List II.

	List I	List II
P.	Monoclinic	1. $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$
Q.	Tetragonal	2. $a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$
R.	Triclinic	3. $a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 90°$
S.	Rhombic	4. $a = b \neq c$, $\alpha = \beta = \gamma = 90°$

	P	Q	R	S
(*a*)	3	4	2	1
(*b*)	4	3	1	2
(*c*)	3	4	1	2
(*d*)	2	3	4	1

2. Match the type of crystal given in List I with example in List II.

	List I	List II
P.	Ionic	1. AlN
Q.	Network	2. Mg
R.	Metallic	3. MgO
S.	Molecular	4. Solid CO_2

	P	Q	R	S
(*a*)	3	1	4	2
(*b*)	3	1	2	4
(*c*)	1	3	2	4
(*d*)	4	2	3	1

3. Match the distribution of particles A and B in List I with formula given in List II.

	List I	List II
P.	A in *ccp* and B equally distributed in octahedral and tetrahedral	1. A_2B_3
Q.	B in *hcp* and A occupy 2/3rd of octahedral voids	2. A_3B
R.	A at the corners and face centres and B at edge centres and body centre	3. AB
S.	B in ccp and A occupy all the octahedral and tetrahedral sites	4. AB_2

	P	Q	R	S
(*a*)	4	1	3	2
(*b*)	4	1	2	3
(*c*)	3	2	1	4
(*d*)	4	2	3	1

4. Match the entries of column I with appropriate entries of column II.

	Compound	Magnetic property
(A)	NaCl	(*p*) Ferrimagnetic
(B)	MnO	(*q*) Paramagnetic
(C)	$CrCl_3$	(*r*) Ferromagnetic
(D)	CrO_2	(*s*) Diamagnetic
(E)	$MgFe_2O_4$	(*t*) Antiferromagnetic

	A	B	C	D	E
(*a*)	*p*	*r*	*q*	*t*	*s*
(*b*)	*t*	*q*	*r*	*p*	*s*
(*c*)	*r*	*t*	*q*	*p*	*s*
(*d*)	*s*	*t*	*q*	*r*	*p*
(*e*)	*s*	*r*	*t*	*q*	*p*

(*Kerala PMT 2015*)

Answers

1. (*c*) **2.** (*b*) **3.** (*a*) **4.** (*d*)

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the given example.

	p	q	r	s
A	p	q	r	s
B	p	q	r	s
C	p	q	r	s
D	p	q	r	s

1. Match the crystal system/unit cells mentioned in column I with their characteristic features mentioned in column II.

Column I	Column II
(A) Simple cubic and face centred cubic	(*p*) have these cells parameters $a = b = c$ and $\alpha = \beta = \gamma$
(B) Cubic and rhombohedral	(*q*) are two crystal systems
(C) Cubic and tetragonal	(*r*) have only two crystallographic angles of 90°
(D) Hexagonal and monoclinic	(*s*) belong to same crystal system.

(*I.I.T. 2007*)

Answers

(1) : (A) – (*p*) (*s*) (B) – (*p*) (*q*) (C) – (*q*) (D) – (*q*) (*r*)

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2. Match the imperfections in solids mentioned in column I with the characteristic features mentioned in column II.

Column I	Column II
(A) Schottky defects	(*p*) excess cations occupy interstitial sites
(B) Frenkel defects	(*q*) conduct electricity due to free electrons
(C) Metal excess defects	(*r*) act as *p*-type semi-conductors
(D) Metal deficient defects	(*s*) are non-stoichiometric defects

3. Match the type of arrangement in column I with the characteristic feature mentioned in column II.

Column I	Column II
(A) Cubic close packing	(*p*) occupy 74% of the space
(B) Hexagonal close packing	(*q*) occupy 68% of the space
(C) Body centred cubic	(*r*) have 1 atom per unit cell
(D) Simple cubic	(*s*) have more number of atoms per unit cell than simple cubic arrangement

Answers

(2) : (A) – (*q*) (B) – (*p*) (*q*) (C) – (*p*) (*q*) (*s*) (D) – (*r*) (*s*)
(3) : (A) – (*p*) (*s*) (B) – (*p*) (*r*) (*s*) (C) – (*s*) (D) – (*q*).

Integer Type and Numerical Value Type Questions

Interger Type: The answer to each of the following question is a **single-digit**-integer ranging from 0 to 9.

1. Silver (atomic weight = 108 g mol^{-1}) has a density of 10.5 g cm^{-3}. The number of silver atoms on a surface of area 10^{-12} m^2 can be expressed in scientific notation as $y \times 10^{x}$. The value of x is *(I.I.T. 2010)*

2. In NaCl structure, Cl^- ions have ccp arrangement and Na^+ ions occupy all the octahedral sites. The total number of Na^+ and Cl^- ions per unit cell is :

3. A metal 'X' crytallizes in a unit cell in which the radius of atom (r) is related to edge of unit cell (a) as $r = 0.3535\,a$. The total number of atoms present per unit cell is

4. The radius ratio of an ionic solid r_+/r_- is 0.524. The coordination number of this type of structure is

5. Atoms of element N form *hcp* arrangement and those of element M occupy 2/3rd of tetrahedral voids. The total number of M and N per formula unit is

6. In hexagonal close packing, the difference in the number of tetrahedral and octahedral voids per unit cell is

7. The ratio of coordination number of each sphere in *ccp* and *hcp* in three dimensions is

8. A compound is formed by two elements X and Y. The element Y form *ccp* and atoms of X occupy 1/3 of tetrahedral voids. If the formula of the compound is $X_a Y_b$, then value of $a + b$ is

9. A cubic unit cell has one atom on each corner and one atom on each body diagonal. The number of atoms in the unit cell is

10. The number of hexagonal faces that are present in a truncated octahedron is *(I.I.T. 2011)*

11. A crystalline solid of a pure substance has a face centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8 g cm^{-3}, then the number of atoms present in 256 g of the crystal is $N \times 10^{24}$. The value of N is

(JEE Advance 2017)

Numerical Value Type: Give the correct numerical value (in decimal notation truncated/rounded off to the second decimal place).

12. Consider an ionic solid MX with NaCl structure. Construct a new structure (Z) whose unit cell is constructed from the unit cell of MX following the sequential instructions given below. Neglect the charge balance.

(1) Remove all the anions (X) except the central one
(2) Replace all the face centred cations (M) by anions (X)
(3) Remove all the corner cations (M)
(4) Replace the central anion (X) with cation (M)

The value of $\left(\frac{\text{number of anions}}{\text{number of cations}}\right)$ in Z is _____

(JEE Advance 2018)

Answers

1. 7 **2.** 8 **3.** 4 **4.** 6 **5.** 7 **6.** 6 **7.** 1 **8.** 5 **9.** 5
10. 8 **11.** 2 **12.** 3.00

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NCERT Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

1. Which of the following conditions favours the existence of a substance in the solid state?
(*a*) High temperature (*b*) Low temperature
(*c*) High thermal energy (*d*) Weak cohesive forces

2. Which of the following is not a characteristic of a crystalline solid ?
(*a*) Definite and characteristic heat of fusion.
(*b*) Isotropic nature.
(*c*) A regular periodically repeated pattern of arrangement of constituent particles in the entire crystal.
(*d*) A true solid

3. Which of the following is an amorphous solid ?
(*a*) Graphite (C) (*b*) Quartz glass (SiO_2)
(*c*) Chrome alum (*d*) Silicon carbide (SiC)

4. Which of the following arrangements shows schematic alignment of magnetic moments of antiferromagnetic substances ?

(*a*) ↑ ↑ ↑ ↑ ↑ ↑
(*b*) ↓ ↓ ↓ ↓ ↓ ↓
(*c*) ↑ ↑ ↓ ↑ ↑ ↓
(*d*) ↑ ↓ ↑ ↓ ↑ ↓

5. Which of the following is true about the value of refractive index of quartz glass?
(*a*) Same in all directions
(*b*) Different in different directions
(*c*) Cannot be measured
(*d*) Always zero

6. Which of the following statement is not true about amorphous solids?
(*a*) On heating they may become crystalline at certain temperature.
(*b*) They may become crystalline on keeping for long time.
(*c*) Amorphous solids can be moulded by heating.
(*d*) They are anisotropic in nature.

7. The sharp melting point of crystalline solids is due to _____.
(*a*) a regular arrangement of constituent particles observed over a short distance in the crystal lattice.
(*b*) a regular arrangement of constituent particles observed over a long distance in the crystal lattice.
(*c*) same arrangement of constituent particles in different directions.
(*d*) different arrangement of constituent particles in different directions.

8. Iodine molecules are held in the crystals lattice by _____.
(*a*) London forces
(*b*) dipole-dipole interactions
(*c*) covalent bonds
(*d*) coulombic forces

9. Which of the following is a network solid?
(*a*) SO_2 (Solid) (*b*) I_2
(*c*) Diamond (*d*) H_2O (Ice)

10. Which of the following solids is not an electrical conductor?
(A) Mg(*s*) (B) TiO(*s*) (C) $I_2(s)$ (D) $H_2O(s)$
(*a*) (A) only (*b*) (B) Only
(*c*) (C) and (D) (*d*) (B), (C) and (D)

11. Which of the following is not the characteristic of ionic solids?
(*a*) Very low value of electrical conductivity in the molten state.
(*b*) Brittle nature.
(*c*) Very strong forces of interactions.
(*d*) Anisotropic nature.

12. Graphite is a good conductor of electricity due to the presence of _____.
(*a*) lone pair of electrons (*b*) free valence electrons
(*c*) cations (*d*) anions

13. Which of the following oxides behaves as conductor or insulator depending upon temperature ?
(*a*) TiO (*b*) SiO_2 (*c*) TiO_3 (*d*) MgO

14. Which of the following oxides shows electrical properties like metals ?
(*a*) SiO_2 (*b*) MgO (*c*) $SO_2(s)$ (*d*) CrO_2

15. The lattice site in a pure crystal cannot be occupied by _____.
(*a*) molecule (*b*) ion
(*c*) electron (*d*) atom

16. Graphite cannot be classified as _____.
(*a*) conducting solid (*b*) network solid
(*c*) covalent solid (*d*) ionic solid

17. Cations are present in the interstitial sites in _____.
(*a*) Frenkel defect (*b*) Schottky defect
(*c*) Vacancy defect (*d*) Metal deficiency defect

18. Schottky defect is observed in crystals when _____.
(*a*) some cations move from their lattice site to interstitial sites.
(*b*) equal number of cations and anions are missing from the lattice.
(*c*) some lattice sites are occupied by electrons.
(*d*) some impurity is present in the lattice.

Answers

1. (*b*)	**2.** (*b*)	**3.** (*b*)	**4.** (*d*)	**5.** (*a*)	**6.** (*d*)	**7.** (*b*)	**8.** (*a*)	**9.** (*c*)	**10.** (*c*)
11. (*a*)	**12.** (*b*)	**13.** (*c*)	**14.** (*d*)	**15.** (*c*)	**16.** (*d*)	**17.** (*a*)	**18.** (*b*)		

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19. Which of the following is true about the charge acquired by *p*-type semiconductors ?
(*a*) positive
(*b*) neutral
(*c*) negative
(*d*) depends on concentration of *p* impurity

20. To get a *n*-type semiconductor from silicon, it should be doped with a substance with valence_____.
(*a*) 2 (*b*) 1 (*c*) 3 (*d*) 5

21. The total number of tetrahedral voids in the face centred unit cell is _____.
(*a*) 6 (*b*) 8 (*c*) 10 (*d*) 12

22. Which of the following point defects are shown by AgBr(*s*) crystals ?
(A) Schottky defect
(B) Frenkel defect
(C) Metal excess defect
(D) Metal deficiency defect
(*a*) (A) and (B) (*b*) (C) and (D)
(*c*) (A) and (C) (*d*) (B) and (D)

23. In which pair most efficient packing is present?
(*a*) *hcp* and *bcc* (*b*) *hcp* and *ccp*
(*c*) *bcc* and *ccp* (*d*) *bcc* and simple cubic cell

24. The percentage of empty space in a body centred cubic arrangement is _____.
(*a*) 74 (*b*) 68
(*c*) 32 (*d*) 26

25. Which of the following statement is not true about the hexagonal close packing ?
(*a*) The coordination number is 12.
(*b*) It has 74% packing efficiency.
(*c*) Tetrahedral voids of the second layer are covered by the spheres of the third layer.
(*d*) In this arrangement spheres of the fourth layer are exactly aligned with those of the first layer.

26. In which of the following structures coordination number for cations and anions in the packed structure will be same?
(*a*) Cl^- ions form *fcc* lattice and Na^+ ions occupy all octahedral voids of the unit cell.
(*b*) Ca^{2+} ions form *fcc* lattice and F^- ions occupy all the eight tetrahedral voids of the unit cell.
(*c*) O^{2-} ions form *fcc* lattice and Na^+ ions occupy all the eight tetrahedral voids of the unit cell.
(*d*) S^{2-} ions form *fcc* lattice and Zn^{2+} ions go into alternate tetrahedral voids of the unit cell.

27. What is the coordination number in a square close packed structure in two dimensions ?
(*a*) 2 (*b*) 3
(*c*) 4 (*d*) 6

28. Which kind of defects are introduced by doping?
(*a*) Dislocation defect
(*b*) Schottky defect
(*c*) Frenkel defects
(*d*) Electronic defects

29. Silicon doped with electron-rich impurity forms _____.
(*a*) *p*-type semiconductor
(*b*) *n*-type semiconductor
(*c*) intrinsic semiconductor
(*d*) insulator

30. Which of the following statements is not true ?
(*a*) Paramagnetic substances are weakly attracted by magnetic field.
(*b*) Ferromagnetic substances cannot be magnetised permanently.
(*c*) The domains in antiferromagnetic substances are oppositely oriented with respect to each other.
(*d*) Pairing of electrons cancels their magnetic moment in the diamagnetic substances.

31. Which of the following is not true about the ionic solids?
(*a*) Bigger ions form the close packed structure.
(*b*) Smaller ions occupy either the tetrahedral or the octahedral voids depending upon their size.
(*c*) Occupation of all the voids is not necessary.
(*d*) The fraction of octahedral or tetrahedral voids occupied depends upon the radii of the ions occupying the voids.

32. A ferromagnetic substance becomes a permanent magnet when it is placed in a magnetic field becuase _____.
(*a*) all the domains get oriented in the direction of magnetic field.
(*b*) all the domains get oriented in the direction opposite to the direction of magnetic field.
(*c*) domains get oriented randomly.
(*d*) domains are not affected by magnetic field.

33. The correct order of the packing efficiency in different types of unit cells is _____.
(*a*) *fcc* < *bcc* < simple cubic
(*b*) *fcc* > *bcc* > simple cubic
(*c*) *fcc* < *bcc* > simple cubic
(*d*) *bcc* < *fcc* > simple cubic

34. Which of the following defects is also known as dislocation defect?
(*a*) Frenkel defect
(*b*) Schottky defect
(*c*) Non-stoichiometric defect
(*d*) Simple interstitial defect

35. In the cubic close packing, the unit cell has _____.
(*a*) 4 tetrahedral voids each of which is shared by four adjacent unit cells.
(*b*) 4 tetrahedral voids within the unit cell.
(*c*) 8 tetrahedral voids each of the which is shared by four adjacent unit cells.
(*d*) 8 tetrahedral voids within the unit cells.

Answers

19. (*b*) **20.** (*d*) **21.** (*b*) **22.** (*a*) **23.** (*b*) **24.** (*c*) **25.** (*d*) **26.** (*a, d*) **27.** (*c*) **28.** (*d*)
29. (*b*) **30.** (*b*) **31.** (*d*) **32.** (*a*) **33.** (*b*) **34.** (*a*) **35.** (*d*)

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36. The edge lengths of the unit cells in terms of the radius of spheres constituting *fcc*, *bcc* and simple cubic unit cell are respectively_____.

(*a*) $2\sqrt{2r}$, $\frac{4r}{\sqrt{3}}$, $2r$ (*b*) $\frac{4r}{\sqrt{3}}$, $2\sqrt{2r}$, $2r$

(*c*) $2r$, $2\sqrt{2r}$, $\frac{4r}{\sqrt{3}}$ (*d*) $2r$, $\frac{4r}{\sqrt{3}}$, $2\sqrt{2r}$

37. Which of the following represents correct order of conductivity in solids?

(*a*) $\kappa_{metals} >> \kappa_{insulators} < \kappa_{semiconductors}$

(*b*) $\kappa_{metals} << \kappa_{insulators} < \kappa_{semiconductors}$

(*c*) $\kappa_{metals} \simeq \kappa_{semiconductors} > \kappa_{insulators} = zero$

(*d*) $\kappa_{metals} < \kappa_{semiconductors} > \kappa_{insulators} \neq zero$

Answers

36. (*a*) **37.** (*a*)

Multiple Choice Questions (Type-II)

Note : *In the following questions two or more options may be correct.*

38. Which of the following is not true about the voids formed in three dimensional hexagonal close packed structure ?

(*a*) A tetrahedral void is formed when a sphere of the second layer is present above triangular void in the first layer.

(*b*) All the triangular voids are not covered by the spheres of the second layer.

(*c*) Tetrahedral voids are formed when the triangular voids in the second layer lie above the triangular voids in the first layer and the triangular shapes of these voids do not overlap.

(*d*) Octahedral voids are formed when the triangular voids in the second layer exactly overlap with similar voids in the first layer.

39. The value of magnetic moment is zero in the case of antiferromagnetic substances because the domains _____.

(*a*) get oriented in the direction of the applied magnetic field.

(*b*) get oriented opposite to the direction of the applied magnetic field.

(*c*) are oppositely oriented with respect to each other without the application of magnetic field.

(*d*) cancel out each other's magnetic moment.

40. Which of the following statements are not true?

(*a*) Vacancy defect results in a decrease in the density of the substance.

(*b*) Interstitial defects results in an increase in the density of the substance.

(*c*) Impurity defect has no effect on the density of the substance.

(*d*) Frenkel defect results in an increase in the density of the substance.

41. Which of the following statements are true about metals ?

(*a*) Valence band overlaps with conduction band.

(*b*) The gap between valence band and conduction band is negligible.

(*c*) The gap between valence band and conduction band cannot be determined.

(*d*) Valence band may remain partially filled.

42. Under the influence of electric field, which of the following statements is true about the movement of electrons and holes in a *p*-type semiconductor?

(*a*) Electron will move towards the positvely charged plate through electron holes.

(*b*) Holes will appear to be moving towards the negatively charged plate.

(*c*) Both electrons and holes appear to move towards the positively charged plate.

(*d*) Movement of electrons is not related to the movement of holes.

43. Which of the following statements are true about semiconductors?

(*a*) Silicon doped with electron rich impurity is a *p*-type semiconductor.

(*b*) Silicon doped with an electron rich impurity is an *n*-type semiconductor.

(*c*) Delocalised electrons increase the conductivity of doped silicon.

(*d*) An electron vacancy increases the conductivity of *n*-type semiconductor.

44. An excess of potassium ions makes KCl crystals appear violet or lilac in colour since _____.

(*a*) some of the anionic sites are occupied by an unpaired electron.

(*b*) some of the anionic sites are occupied by a pair of electrons.

(*c*) there are vacancies at some anionic sites.

(*d*) F-centres are created which impart colour to the crystals.

45. The number of tetrahedral voids per unit cell in NaCl crystal is _____.

(*a*) 4

(*b*) 8

(*c*) twice the number of octahedral voids.

(*d*) four times the number of octahedral voids.

Answers

38. (*c*), (*d*) **39.** (*c*), (*d*) **40.** (*c*), (*d*) **41.** (*a*), (*b*), (*d*) **42.** (*a*), (*b*) **43.** (*b*), (*c*) **44.** (*a*), (*d*) **45.** (*b*), (*c*)

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46. Amorphous solid can also be called _____.
(*a*) pseudo solids (*b*) true solids
(*c*) super cooled liquids (*d*) super cooled solids

47. A perfect crystal of silicon (Fig.1) is doped with some elements as given in the options. Which of these options show *n*-type semiconductors?

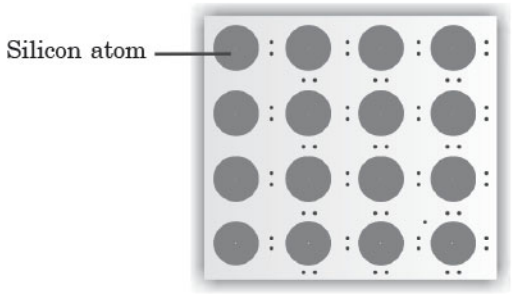
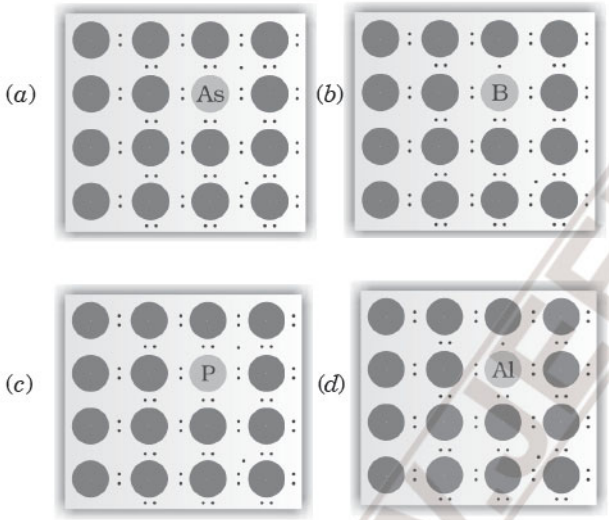


Fig. 1. Pure crystal



48. Which of the following statements are correct?
(*a*) Ferrimagnetic substances lose ferrimagnetism on heating and become paramagnetic.
(*b*) Ferrimagnetic substances do not lose ferrimagnetism on heating and remain ferrimagnetic.
(*c*) Antiferromagnetic substances have domain structures similar to ferromagnetic substances and their magnetic moments are not cancelled by each other.
(*d*) In ferromagnetic substances all the domains get oriented in the direction of magnetic field and remain as such even after removing magnetic field.

49. Which of the following features are not shown by quartz glass?
(*a*) This is a crystalline solid.
(*b*) Refractive index is same in all the directions.
(*c*) This has definite heat of fusion.
(*d*) This is also called super cooled liquid.

50. Which of the following cannot be regarded as molecular solid?
(*a*) SiC (Silicon carbide) (*b*) AlN
(*c*) Diamond (*d*) I_2

51. In which of the following arrangements octahedral voids are formed?
(*a*) *hcp* (*b*) *bcc*
(*c*) simple cubic (*d*) *fcc*

52. Frenkel defect is also known as _____.
(*a*) stoichiometric defect
(*b*) dislocation defect
(*c*) impurity defect
(*d*) non-stoichometric defect

53. Which of the following defects decrease the density?
(*a*) Interstitial defect (*b*) Vacancy defect
(*c*) Frenkel defect (*d*) Schottky defect

Answers

46. (*a*), (*c*) **47.** (*a*), (*c*) **48.** (*a*), (*d*) **49.** (*a*), (*c*) **50.** (*a*), (*b*), (*c*) **51.** (*a*), (*d*) **52.** (*a*), (*b*) **53.** (*b*), (*d*)

Matching Type Questions

Note : *In the following questions match the items given in Column I with the items given in Column II. In some questions more than one item of Column I and Column II may match.*

54. Match the defects given in Column I with the statements in given Column II.

Column I	*Column II*
(*a*) Simple vacancy defect	(*i*) shown by non-ionic solids and increases density of the solid.
(*b*) Simple interstitial defect	(*ii*) shown by ionic solids and decreases density of the solid.
(*c*) Frenkel defect	(*iii*) shown by non ionic solids and density of the solid decreases.
(*d*) Schottky defect	(*iv*) shown by ionic solids and density of the solid remains the same.

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55. Match the type of unit cell given in Column I with the features given in Column II.

Column I	Column II
(*a*) Primitive cubic unit cell.	(*i*) Each of the three perpendicular edges compulsorily have the different edge length *i.e.*, $a \neq b \neq c$.
(*b*) Body centred cubic unit cell.	(*ii*) Number of atoms per unit cell is one.
(*c*) Face centred cubic unit cell.	(*iii*) Each of the three perpendicular edges compulsorily have the same edge length *i.e.*, $a = b = c$.
(*d*) End centred orthorhombic.	(*iv*) In addition to the contribution from unit cell the corner atoms the number of atoms present in a unit cell is one.
	(*v*) In addition to the contribution from the corner atoms the number of atoms present in a unit cell is three.

56. Match the types of defect given in Column I with the statement given in Column II.

Column I	Column II
(*a*) Impurity defect.	(*i*) NaCl with anionic sites called F-centres.
(*b*) Metal excess defect.	(*ii*) FeO with Fe^{3+}.
(*c*) Metal deficiency defect.	(*iii*) NaCl with Sr^{2+} and some cationic sites vacant.

57. Match the items given in Column I with the items given in Column II.

Column I	Column II
(*a*) Mg in solid state.	(*i*) *p*-Type semiconductor.
(*b*) $MgCl_2$ in molten state.	(*ii*) *n*-Type semiconductor.
(*c*) Silicon with phosphorus.	(*iii*) Electrolytic conductors.
(*d*) Germanium with boron.	(*iv*) Electronic conductors.

58. Match the type of packing given in Column I with the items given in Column II.

Column I	Column II
(*a*) Square close packing in two dimensions.	(*i*) Triangular voids.
(*b*) Hexagonalclose packing in two dimensions.	(*ii*) Pattern of spheres is repeated in every fourth layer.
(*c*) Hexagonal close packing in three dimensions.	(*iii*) Coordination number 4.
(*d*) Cubic close packing in three dimensions.	(*iv*) Pattern of sphere is repeated in alternate layers.

Answers

54. (*a*)–(*iii*); (*b*)–(*i*); (*c*)–(*iv*); (*d*)–(*ii*) **55.** (*a*)–(*ii, iii*); (*b*)–(*iii, iv*); (*c*)–(*iii, v*); (*d*)–(*i, iv*) **56.** (*a*)–(*iii*); (*b*)–(*i*); (*c*)–(*ii*)
57. (*a*)–(*iv*); (*b*)–(*iii*); (*c*)–(*ii*); (*d*)–(*i*) **58.** (*a*)–(*iii*); (*b*)–(*i*); (*c*)–(*iv*); (*d*)–(*ii*)

Assertion and Reason Type Questions

Note : *In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.*

(*a*) *Assertion and reason both are correct statements and reason is correct explanation for assertion.*
(*b*) *Assertion and reason both are correct statements but reason is not correct explanation for assertion.*
(*c*) *Assertion is correct statement but reason is wrong statement.*
(*d*) *Assertion is wrong statement but reason is correct statement.*

59. Assertion : The total number of atoms present in a simple cubic unit cell is one.
Reason : Simple cubic unit cell has atoms at its corners, each of which is shared between eight adjacent unit cells.

60. Assertion : Graphite is a good conductor of electricity however diamond belongs to the category of insulators.
Reason : Graphite is soft in nature on the other hand diamond is very hard and brittle.

61. Assertion : Total number of octahedral voids present in unit cell of cubic close packing including the one that is present at the body centre, is four.
Reason : Besides the body centre there is one octahedral void present at the centre of each of the six faces of the unit cell and each of which is shared between two adjacent unit cells.

62. Assertion : The packing efficiency is maximum for the *fcc* structure.
Reason : The cordination number is 12 in *fcc* structures.

63. Assertion : Semiconductors are solids with conductivities in the intermediate range from 10^{-6} – 10^{4} $ohm^{-1}m^{-1}$.
Reason : Intermediate conductivity in semiconductor is due to partially filled valence band.

Answers

59. (*a*) **60.** (*b*) **61.** (*c*) **62.** (*b*) **63.** (*c*)

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Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A8. (*c*) : $a = 2\sqrt{2}\ r$

$= 2 \times 1.414 \times 141.5 = 400$ pm

Volume of unit cell

$= (400 \times 10^{-10}\ \text{cm})^3 = 6.4 \times 10^{-23}\ \text{cm}^3$

No. of unit cells in 64 cm^3

$= \dfrac{64}{6.4 \times 10^{-23}} = 1 \times 10^{24}$ unit cells

A9. (*c*) : For simple cubic, distance between nearest neighbours = a

Empty space = 0

For *fcc* distance between nearest neighbours,

$$d = \frac{a}{\sqrt{2}}$$

$$\text{Empty space} = a - \frac{a}{\sqrt{2}} = a\left(1 - \frac{1}{\sqrt{2}}\right)$$

For *bcc*, $d = \dfrac{\sqrt{3}a}{2}$

$$\text{Empty space} = a - \frac{\sqrt{3}a}{2} = a\left(1 - \frac{\sqrt{3}}{2}\right)$$

A10. (*c*) : No of atoms present in *fcc* unit cell = 4

Total volume of atoms present in *fcc* unit cell

$$= 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$$

A14. (*b*) : In *bcc*, radius of atom,

$$r = \frac{\sqrt{3}a}{4}$$

where a is the edge length

The edge length not covered by atoms = $a - 2r$

$$= a - 2 \times \frac{\sqrt{3}}{4}a = a\left(\frac{2 - \sqrt{3}}{2}\right)$$

$$= \frac{a(2 - 1.732)}{2} = 0.134a$$

Percentage of edge length not covered

$$= \frac{0.134a}{a} \times 100 = 13.4\%$$

A15. (*c*) : $r = \dfrac{a}{2\sqrt{2}} = \dfrac{620}{2 \times 1.414} = 219.20$ pm

A16. (*a*) : No. of NaCl molecules in a unit cell = 4

$$\text{Mass of unit cell} = \frac{4 \times 58.5}{6.022 \times 10^{23}}$$

$$\text{No. of unit cells in 1g} = \frac{1 \times 6.022 \times 10^{23}}{4 \times 58.5} = 2.57 \times 10^{21}$$

A18. (*a*) : No. of A atoms per unit cell = 8 (at corners) $\times \dfrac{1}{8}$

$= 1$

No. of B atoms per unit cell

$= 6$ (at the face centre) $\times \dfrac{1}{2} = 3$

Formula AB_3

A20. (*d*) : $d = \dfrac{Z \times M}{a^3 \times N_A}$

$$2.7 = \frac{Z \times 27}{\left(405 \times 10^{-10}\right)^3 \times \left(6.02 \times 10^{23}\right)}$$

$$\text{or} \quad Z = \frac{2.7 \times \left(405 \times 10^{-10}\right)^3 \times 6.02 \times 10^{23}}{27} = 4$$

$\therefore$ Lattice is *fcc*.

A21. (*a*) : No. of O^{2-} ions in *ccp* = 4

There will be 8 tetrahedral sites and 4 octahedral sites

No. of Fe^{2+} ions $= \dfrac{1}{8} \times 8 = 1$

No. of Fe^{3+} ions $= \dfrac{1}{8} \times 8 + \dfrac{1}{4} \times 4 = 2$

Formula of magnetite : $Fe^{2+}\ Fe_2^{3+} O_4^{2-} \equiv Fe_3O_4$

A22. (*c*) : No. of Cu atoms = 4 (*ccp* arrangement)

No. of Ag atoms = 12 (edges) $\times \dfrac{1}{4} = 3$

No. of Au atoms = 1 (body centre)

Formula $Cu_4\ Ag_3\ Au$

A23. (*b*) : No. of O^{2-} ions in *ccp* arrangement = 4

No. of octahedral holes = 4

No. of B^{3+} ions $= 4 \times \dfrac{1}{2} = 2$

No. of tetrahedral holes = $4 \times 2 = 8$

No. of A^{2+} ions $= 8 \times \dfrac{1}{8} = 1$

Formula $A\ B_2O_4$

A24. (*c*) : No. of W atoms per unit cell = 1

No. of O atoms per unit cell $= 12 \times \dfrac{1}{4}$ (edge centre)

$= 3$

No. of Na atoms per unit cell = 1 (cube centre)

Formula $NaWO_3$

A25. (*c*) : No of Ca atoms per unit cell = 8 (corners) $\times \dfrac{1}{8} = 1$

O atoms per unit cell = 6 (face centres) $\times \dfrac{1}{2} = 3$

Ti atoms per unit cell = 1

$\therefore$ Formula of mineral = $Ca\ TiO_3$

Suppose oxidation state of Ti be x

$+2 + x + 3(-2) = 0$ or $x = +4$

A26. (*d*) : No. of atoms per unit cell of hexagonal primitive unit cell = 6

No of tetrahedral holes = $6 \times 2 = 12$

No. of octahedral holes = $6 \times 1 = 6$

A28. (*d*) : No. of atoms at the corners = 6

Contribution of each atom = 1/8

$\therefore$ No. of P atoms $= 6 \times \dfrac{1}{8} = 3/4$

No. of atoms at the faces = 6

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Contribution of each atom = 1/2

$\therefore$ No. of Q atoms = $6 \times \frac{1}{2} = 3$

Formula $P_{\frac{3}{4}}Q_3$ or PQ_4

A29. (*d*) Molar volume from pyknometer density

$$= \frac{M}{2.165 \times 10^3} \text{ m}^3$$

Molar volume from X-ray density

$$= \frac{M}{2.178 \times 10^3} \text{ m}^3$$

$$\therefore \text{Volume unoccupied} = \frac{M}{10^3}\left[\frac{1}{2.165} - \frac{1}{2.178}\right]\text{m}^3$$

$$= \frac{0.013\,M \times 10^{-3}}{2.165 \times 2.178}$$

$$\therefore \text{Fraction unoccupied} = \frac{0.013\,M \times 10^{-3}}{2.165 \times 2.178} \Big/ \frac{M \times 10^3}{2.165}$$

$$= \mathbf{5.96 \times 10^{-3}}.$$

A30. (*c*) : No. of 'A' atoms = $\frac{1}{8} \times 8 = 1$

No. of 'B' atoms = $1 \times 1 = 1$

No. of 'C' atoms = $\frac{1}{4} \times 12 = 3$

Formula = ABC_3

A31. (*c*) : $d = \frac{Z \times M}{a^3 \times N_A}$

$$11.2 = \frac{4 \times M}{\left(400 \times 10^{-10}\right)^3 \times \left(6.02 \times 10^{23}\right)}$$

or $M = \frac{11.2 \times \left(400 \times 10^{-10}\right)^3 \times \left(6.02 \times 10^{23}\right)}{4} = 107.8$

A32. (*c*) : $d = \frac{Z \times M}{a^3 \times N_A}$

$$6.23 = \frac{4 \times 60}{a^3 \times 6.02 \times 10^{23}}$$

$$a^3 = \frac{4 \times 60}{6.23 \times 6.02 \times 10^{23}} = 64 \times 10^{-24}$$

$$a = 4 \times 10^{-8} \text{ cm} = 400 \text{ pm}$$

A33. (*d*) : Volume of unit cell = $(100 \times 10^{-10} \text{ cm})^3$

$= 10^{-24} \text{ cm}^3$

Mass of unit cell = $V \times d = 10^{-24} \times 10.0 = 10^{-23}$ g

No. of unit cells in 100 g = $\frac{100}{10^{-23}} = 10^{25}$

Since lattice is fcc and each unit cell has 4 atoms per unit cell.

No. of atoms = 4×10^{25}.

A34. (*c*) : For *fcc*, $r = \frac{a}{2\sqrt{2}}$

or $a = 2\sqrt{2}\,r = 2 \times 1.414 \times 128$

$= 362$ pm

$$d = \frac{Z \times M}{a^3 \times N_A}$$

$$= \frac{4 \times 63.5}{\left(362 \times 10^{-10}\right)^3 \times \left(6.02 \times 10^{23}\right)}$$

$= 8.9 \text{ g cm}^{-3}$

A38. (*c*) : $d = \frac{Z \times M}{a^3 \times N_A}$

$$4 = \frac{Z \times 72}{\left(5 \times 10^{-8}\right)^3 \times \left(6.02 \times 10^{23}\right)}$$

or $Z = \frac{4 \times \left(5 \times 10^{-8}\right)^3 \times \left(6.02 \times 10^{23}\right)}{72} = 4$

No. of Fe^{2+} and O^{2-} ions present in each unit cell = 4

B. *mcq from Competitive Examinations*

B1. (*b*) : One cation of Sr^{2+} would create one cation vacancy in NaCl. Therefore, the number of cation vacancies created in the lattice of NaCl is equal to the number of divalent Sr^{2+} ions added.

No. of moles of cationic vacancies

$$= \frac{10^{-4}}{10^2} = 10^{-6} \text{ mol}$$

No. of cation vacancies

$= 10^{-6} \times 6.02 \times 10^{23}$

$= 6.02 \times 10^{17}$

B2. (*d*) : Packing fraction of a simple cube

$$= \frac{\text{Volume of one sphere}}{\text{Volume of cubic unit cell}}$$

Edge length $a = 2r$ or $r = a/2$

$$\therefore \text{Packing fraction} = \frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6}.$$

B3. (*a*) : For simple cubic, $a = 2r$ $\therefore$ $r = \frac{a}{2}$

For *bcc*, $4r = \sqrt{3}a$ $\therefore$ $r = \frac{\sqrt{3}a}{4}$

For *fcc*, $4r = \sqrt{2}a$ $\therefore$ $r = \frac{\sqrt{2}a}{4}$

Ratio is : $\frac{a}{2} : \frac{\sqrt{3}a}{4} : \frac{\sqrt{2}a}{4}$

or $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$

B4. (*a*) : For *bcc* structure,

$$r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 351 = 151.98 \text{ pm}$$

B5. (*a*) : For *fcc* lattice, radius (r) is related to edge length (a)

$$r = \frac{a}{2\sqrt{2}}; \quad a = 408 \text{ pm}$$

$$r = \frac{408}{2 \times 1.414} = 144 \text{ pm}$$

$\therefore$ Diameter = $2 \times 144 = 288$ pm

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B6. (*a*) : $d = \dfrac{Z \times M}{a^3 \times N_A}$

$d = 2.72\ g\ cm^{-3}$, $Z = 4$,
$a = 404\ pm = 4.04 \times 10^{-8}\ cm$

$$2.72 = \frac{4 \times M}{(4.04 \times 10^{-8})^3 \times 6.02 \times 10^{23}}$$

or $M = 27\ g\ mol^{-1}$

B7. (*d*) : Carbon has structure similar to ZnS (zinc blende). Carbon forming *fcc* or *ccp* and also occupying half tetrahedral sites.
Total no. of carbon atoms = $8 \times \frac{1}{8}$ (corners) + $6 \times \frac{1}{2}$
(faces) + 4 (tetrahedral sites) = 8.

B8. (*d*) : The distance between body centred atom and one corner atom is $\frac{\sqrt{3}\,a}{2}$ (*i.e.* half of body diagonal)

B9. (*b*) : In *bcc* arrangement, volume of space occupied = 68%
$\therefore$ Vacant space = 100 – 68 = 32%

B11. (*d*) : For Z = 4, structure is *fcc*

$$r = \frac{\sqrt{2}a}{4} = \frac{1.414 \times 361}{4} = 127\ pm$$

B12. (*d*) : $\rho = \dfrac{Z \times M}{a^3 \times N_A}$

For *bcc*, $Z = 2$, $M = 6.94\ g\ mol^{-1}$

$$\rho = 530\ kg\ m^{-3} = \frac{530\ g \times 10^3}{cm^3 \times 10^6} = 0.530\ g\ cm^{-3}$$

$$0.53 = \frac{2 \times 6.94}{a^3 \times 6.02 \times 10^{23}}$$

$$a^3 = \frac{2 \times 6.94}{0.53 \times 6.02 \times 10^{23}} = 43.5 \times 10^{-24}\ cm^3$$

$\therefore$ $a = 3.52 \times 10^{-8}\ cm = 352\ pm$

B13. (*c*) : $\dfrac{r_+}{r_-} = \dfrac{0.98 \times 10^{-10}\ m}{1.81 \times 10^{-10}\ m} = 0.54$

Since the radius ratio lies between 0.414 – 0.732, its coordination number is 6.

B15. (*c*) : In Frenkel defect the size of cation should be smaller than that of anion.

(*d*) : is also incorrect because $Fe_{0.93}O$ is metal deficient non-stoichiometric compound.

B16. (*c*) : For bcc structure : $4r = \sqrt{3}\,a$

or $a = \dfrac{4r}{\sqrt{3}}$

$Z = 2$

For fcc structure : $4r = \sqrt{2}a$

$a = \dfrac{4r}{\sqrt{2}}$

$Z = 4$

$$\frac{d(bcc)}{d(fcc)} = \frac{\frac{Z(bcc) \times M}{a^3 \times N_A}}{\frac{Z(fcc) \times M}{a^3 \times N_A}} = \frac{\frac{2 \times M}{\left(\frac{4r}{\sqrt{3}}\right)^3 \times N_A}}{\frac{4 \times M}{\left(\frac{4r}{\sqrt{2}}\right)^3 \times N_A}}$$

$$= \frac{2 \times M}{\left(\frac{4r}{\sqrt{3}}\right)^3 \times N_A} \times \frac{\left(\frac{4r}{\sqrt{2}}\right)^3 \times N_A}{4 \times M}$$

$$= \frac{1}{2}\left(\frac{3}{2} \times \frac{\sqrt{3}}{\sqrt{2}}\right) = \frac{3\sqrt{3}}{4\sqrt{2}}$$

B17. (*c*) : For 1 mol of a compound, number of tetrahedral and octahedral voids = 2 + 1 = 3
$\therefore$ No. of voids = $3 \times 0.5 \times 6.022 \times 10^{23} = 9.033 \times 10^{23}$

B18. (*c*) : AgBr shows both Schottky and Frenkel defects

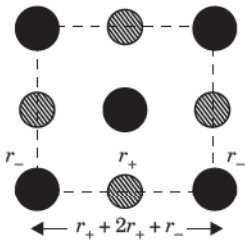
B19. (*c*) : Let x atoms of Fe^{3+} ions are present. This means x Fe^{3+} ions have been replaced by Fe^{2+} ions.
No. of Fe^{2+} ions = $0.93 - x$
For electrical neutrality,
$2(0.93 - x) + 3x = 2$
$1.86 + x = 2$ or $x = 0.14$
Fraction of $Fe^{3+} = 0.14$, $Fe^{2+} = 0.93 - 0.14 = 0.79$
Formula : $Fe^{2+}_{0.79}\ Fe^{3+}_{0.14}\ O^{2-}_{1.0}$
Total molar mass = $0.93 \times 56 + 1 \times 16 = 68.08$

$$\% \text{ of Fe (III)} = \frac{0.14 \times 56}{68.08} \times 100 = 11.5\%$$

B20. (*b*) : No. of Y atoms in a unit cell = 4
No. of tetrahedral sites = $4 \times 2 = 8$
No. of X atoms in unit cell = $8 \times \frac{2}{3} = \frac{16}{3}$
Formula : $X_{\frac{16}{3}}Y_4$ or $X_{\frac{1}{3}}Y_{\frac{1}{4}}$ or X_4Y_3

B21. (*b*) : For *fcc*

$a = 2r_+ + 2r_-$
$a = 2(r_+ + r_-)$



or $r_+ + r_- = \dfrac{a}{2}$

$$r_- = \frac{a}{2} - r_+ = \frac{508}{2} - 110 = 144\ pm$$

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B22. (*d*) : Percentage of free space in *ccp* = 26% and in *bcc* = 32%.

B23. (*d*) : No. of 'A' atoms at corners = $8\times\frac{1}{8}=1$

No. of 'B' atoms at face centres = $5\times\frac{1}{2}=\frac{5}{2}$

Formula = $AB_{5/2}$ or A_2B_5

B24. (*b*) : In a *fcc* lattice

$$4r = \sqrt{2}a$$

$$r=\frac{\sqrt{2}a}{4}=\frac{1.414\times361}{4}=127.61 \simeq \mathbf{128\ pm}$$

B25. (*c*) : For *bcc* structure,

$$r=\frac{a\sqrt{3}}{4}=\frac{351\times1.732}{4}=152\text{ pm}$$

B26. (*c*) : Let fraction of metal which exits as M^{3+} be x

Fraction of metal as $M^{2+} = 0.98 - x$

$\therefore\ 3x + 2(0.98 - x) = 2$

$x + 1.96 = 2$ or $x = 0.04$

$$\%\text{ of } M^{3+}=\frac{0.04}{0.98}\times100=4.08$$

B27. (*d*) : Body diagonal = $\sqrt{3}\,a$

or $2r_{Cs^+} + 2r_{Cl^-} = \sqrt{3}\,a$

$$\therefore\quad r_{Cs^+}+r_{Cl^-}=\frac{\sqrt{3}\,a}{2}$$

B28. (*c*) : For *bcc* lattice,

$$r=\frac{\sqrt{3}a}{4}=\frac{1.732\times4.29}{4}=1.86\text{ Å}$$

B29. (*b*) : CrO_2 is metallic and ferromagnetic.

B30. (*d*) : In *fcc*, the closest approach distance between two atoms,

$$d=\frac{a}{\sqrt{2}}$$

B31. (*c*) : In Frenkel defect, the cations are dislocated from their normal sites to interstitial sites.

B33. (*b*) : Atoms of X per unit cell = $8\times\frac{1}{8}=1$

Atoms of Y per unit cell = 1

Atoms of Z per unit cell = $6\times\frac{1}{2}=3$

$\therefore$ Formula of the compound is XYZ_3.

B34. (*a*) : $\frac{r_{Na^+}}{r_{Cl^-}}=0.55,\qquad \frac{r_{K^+}}{r_{Cl^-}}=0.74$

or $\frac{r_{Na^+}}{r_{Cl^-}}+1=0.55+1,\qquad \frac{r_{K^+}}{r_{Cl^-}}=0.74+1$

$$\frac{r_{Na^+}+r_{Cl^-}}{r_{Cl^-}}=1.55,\qquad \frac{r_{K^+}+r_{Cl^-}}{r_{Cl^-}}=1.74$$

Edge length ratio is

$$\frac{r_{K^+}+r_{Cl^-}}{r_{Cl^-}}\times\frac{r_{Cl^-}}{r_{Na^+}+r_{Cl^-}}=\frac{1.74}{1.55}\Rightarrow\frac{r_{K^+}+r_{Cl^-}}{r_{Na^+}+r_{Cl^-}}=1.122$$

B36. (*a*) : Each unit cell is surrounded by 6 other unit cells because a *fcc* unit cell has six faces.

B39. (*a*) : $\text{Density}=\frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$

$$=\frac{\text{No. of atoms}\times\text{Mass of each atom}}{\text{Volume of unit cell}}$$

For *fcc*, no. of atoms per unit cell = 4

$$\text{Density}=\frac{4\times m}{a^3}$$

B41. (*c*) : In Schottky defect equal number of cations and anions are missing from their lattice sites.

B42. (*c*) : No. of atoms in *fcc* unit cell = 4

Volume occupied by 1 atom = $\frac{4}{3}\pi r^3$

Volume occupied by 4 atoms = $4\times\frac{4}{3}\pi r^3=\frac{16}{3}\pi r^3$

B43. (*d*) : $\rho-\frac{Z\times M}{a^3\times N_A}$

For *bcc*, Z = 2, $a = 500\times10^{-10}$ cm

$d = 4\text{ g cm}^{-3}$

$$4=\frac{2\times M}{\left(500\times10^{-10}\right)^3\times\left(6\times10^{23}\right)}$$

$$M=\frac{4\times\left(500\times10^{-10}\right)^3\times6\times10^{23}}{2}$$

$= 150\text{ g mol}^{-1}$

B44. (*b*) : Each particle at the edge centre is surrounded by four unit cells. Therefore, its contribution per unit cell is $\frac{1}{4}$.

B45. (*b*) : Frenkel defect is a dislocation defect.

B46. (*a*) : The dimensions; $\alpha\neq\beta\neq\gamma\neq90°$ and $a\neq b\neq c$ represent triclinic crystal system. Among the given options only $K_2Cr_2O_7$ exhibits triclinic crystal system.

B47. (*b*) : No. of A atoms at the corners = $7\times\frac{1}{8}=\frac{7}{8}$

No. of B atoms at face centres = $6\times\frac{1}{2}=3$

Ratio of A : B = $\frac{7}{8}:3$

Formula of compound is A_7B_{24}

B48. (*a*) : No. of X atoms = $8\times\frac{1}{8}=1$

No. of Y atoms = 1

Formula : XY

B49. (*c*) : Length of body diagonal $=\sqrt{3}.a$

$= 1.732\times300$

$= 519.6$ pm

B51. (*d*) : No. of atoms (A) on the corners = 8

No. of atoms (A) on the face centres = 6

Removing face centred atoms along one of the axes means removal of 2A atoms so that

No. of A atoms per unit cell = $8\times\frac{1}{8}+4\times\frac{1}{2}=3$

No. of B atoms per unit cell in NaCl type structure = 4

Formula = A_3B_4

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B52. (*b*) : In ZnS, S^{2-} ions are present in all the corners and centres of each face (*fcc* or *ccp* arrangement). Zn^{2+} ions occupy alternate tetrahedral sites.

B53. (*d*) : Packing efficiency = $\frac{\text{Area covered by particles}}{\text{Total area}}$

If a is the length of unit cell

Face diagonal, AC = $\sqrt{2}\,a$

But $AC = 4r$

$\therefore \quad \sqrt{2}\,a = 4r$

$a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}r$

No. of particles $= 4\times\frac{1}{4}+1 = 2$

Area occupied by particles $= 2 \times \pi r^2$

$\therefore$ Packing efficiency $= \frac{2\times\pi r^2}{(2\sqrt{2}r)^2} = \frac{\pi}{4}$

$= 0.7857$ or $78.57\ \%$.

B54. (*b*) : X are present at all the corners and face centres

No. of X atoms $= 8\times\frac{1}{8}+6\times\frac{1}{2} = 4$

M are present at 4 edges and at body centre

No. of M atoms $= 4\times\frac{1}{4}+1\times1 = 2$

The empirical formula of compound : M_2X_4 or MX_2

B55. (*a*) : Cation A^+ occupies octahedral void of arrangement of X^- anions

$\frac{r_{A^+}}{r_{X^-}} = 0.414 \Rightarrow \frac{r_{A^+}}{250} = 0.414$

or $r_{A^+} = 0.414 \times 250 = 104$ pm.

B56. (*a*) : For *ccp* arrangement, Z = 4

$\therefore$ No. of O atoms = 4

No. of octahedral voids = 4

No. of tetrahedral voids = $4 \times 2 = 8$

No. of Al^{3+} ions = $m \times 4$

No. of Mg^{2+} ions = $n \times 8$

Thus the formula of mineral is

$Al_{4m}\ Mg_{8n}\ O_4$

$4m(+3) + 8n(+2) + 4(-2) = 0$

$12\,m + 16\,n - 8 = 0$

$4(3m + 4n - 2) = 0$

$\therefore \quad 3m + 4n = 2$

Possible values of m and n are

$3\times\frac{1}{2}+4\times\frac{1}{8} = 2$ true

$3\times1+4\times\frac{1}{4} = 2$ not true

$3\times\frac{1}{2}+4\times\frac{1}{2} = 2$ not true

$3\times\frac{1}{4}+4\times\frac{1}{8} = 2$ not true

C. mcq with more than one correct answer

C1. (*c,d*) : A hexagonal close packing has coordination number 12 and is not as closely packed as *bcc*.

C2. (*a,c,d*) : (*b*) is not correct because it has coordination number 8.

C3. (*a,b,c*) : $Cs^+(8), Cl^-(8); Na^+(6); Cl^-(6); Zn^{2+}(4), S^{2-}(4); Na^+(4), O^{2-}(8)$.

C9. (*b,c*) : ZnS shows Frenkel defect while AgBr shows both Frenkel and Schottky defects. Therefore, options (*b*) and (*c*) are correct.

D. mcq based on passage/comprehension

Passage I.

D1. (*b*) : The number of atoms per unit cell in different types of unit cells are :

$f = 4$, $b = 2$, $e = 2$ and $s = 1$

D2. (*c*) : From geometry we can prove that, $r = \frac{a}{2\sqrt{2}}$

$\therefore \quad r = \frac{0.410}{2\times1.414} = 0.145$ nm

D3. (*d*) : No. of X atoms $= 7 \times \frac{1}{8} = 7/8$

No. of Y atoms $= 1 \times \frac{1}{8} = 1/8$

No. of Z atoms $= 6 \times \frac{1}{2} = 3$

Formula $= X_{7/8}\,Y_{1/8}\,Z_3 = X_7YZ_{24}$

D4. (*a*) : $\frac{r(Rb^+)}{r(Br^-)} = \frac{148}{195} = 0.76$ (C.N. 8 above 0.732)

$\frac{r(K^+)}{r(Br^-)} = \frac{137}{195} = 0.702$

(C.N. 6 between 0.414 – 0.732)

D5. (*c*) : *fcc* arrangement has 4 atoms per unit cell while *bcc* arrangement has 2 atoms per unit cell. Therefore, ratio between atoms is 4 : 2 or 2 : 1. Here density does not make any difference.

Passage II.

D6. (*b*) : Vol. of unit cell $= (100 \times 10^{-10}\ \text{cm})^3$

$= 1 \times 10^{-24}\ \text{cm}^3$

Mass of an atom $= \frac{24.0}{24\times10^{23}} = 1 \times 10^{-23}$ g

(No. of atoms in *fcc* = 4)

Mass of unit cell $= 4 \times 1 \times 10^{-23} = 4 \times 10^{-23}$ g

Density $= \frac{4\times10^{-23}}{1\times10^{-24}} = \mathbf{40\ g\ cm^{-3}}$

D7. (*c*) : Vol. of unit cell $= (200 \times 10^{-10})^3 = 8 \times 10^{-24}$ cm^3

Volume of 100 g of element $= \frac{100}{12.5} = 8\ \text{cm}^3$

No. of unit cell $= \frac{8}{8\times10^{-24}} = 1 \times 10^{24}$

No. of atoms in 100 g $= 2 \times 1 \times 10^{24} = \mathbf{2 \times 10^{24}}$

(No. of atoms in *bcc* unit cell = 2)

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D8. (*b*) : $\text{Mass of unit cell} = \frac{2\times60}{6.02\times10^{23}}$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$4.2 = \frac{2\times60}{6.02\times10^{23}\times V}$$

$$\text{or } V = \frac{2\times60}{6.02\times10^{23}\times4.2} = \mathbf{4.75\times10^{-23}\ cm^3.}$$

Passage III.

D9. (*b*) : Effective no. of atoms present in unit cell of *hcp*

$$= 2\times\frac{1}{2} + 3\times1 + 12\times\frac{1}{6} = 6$$

D10. (*a*) : Volume = Base area × Height

$$= 6\times\frac{\sqrt{3}}{4}a^2\times2\times\sqrt{\frac{2}{3}}a$$

Putting $a = 2r$

$$6\times\frac{\sqrt{3}}{4}(2r)^2\times2\times\sqrt{\frac{2}{3}}.2r$$

$$= 6\times\frac{\sqrt{3}}{4}\times4r^2\times2\sqrt{\frac{2}{3}}.2r = 24\sqrt{2}r^3$$

D11. (*d*) : Packing fraction in *hcp* = 0.74

∴ Void fraction = 1 – 0.74 = 0.26

∴ Empty space in *hcp* unit cell = 26%.

Assertion Reason Type Questions

2. (*e*) : **Correct assertion :** ZnS has *fcc* structure.
Correct reason : S^{2-} ions adopt *ccp* or *fcc* arrangement and Zn^{2+} ions occupy alternate tetrahedral sites.

3. (*c*) : **Correct reason :** Cl^- ions in CsCl have simple cubic arrangement.

5. (*a*) : Both assertion and reason are correct.

6. (*c*) : **Correct reason :** Since there are two tetrahedral sites for each Ca^{2+} ion, the number of F^- ions are double the number of Ca^{2+} ions.

7. (*e*) : **Correct assertion :** Octahedral void is larger in size than tetrahedral void.
Correct reason : Cations are generally smaller than anions and therefore occupy less space.

8. (*a*) : Both assertion and reason are correct.

9. (*a*) : Both assertion and reason are correct.

10. (*c*) : **Correct reason :** In Frenkel and Schottky defect, the number of cations and anions remains the same.

Integer Type or Numerical Value Type Questions

1. (7) : $\text{Density} = \frac{\text{Mass}}{\text{Volume}}$

10.5 g/cm^3 means in 1 cm^3 Ag = 10.5 g

$$\text{No. of atoms in 1 cm}^3 = \frac{10.5}{108}N_A$$

$$\text{No. of atoms in 1 cm} = \left(\frac{10.5}{108}N_A\right)^{1/3}$$

$$\text{No. of atoms in 1 cm}^2 = \left(\frac{10.5}{108}N_A\right)^{2/3}$$

No. of atoms in 10^{-12} m^2 or 10^{-8} cm^2

$$= \left(\frac{10.5}{108}N_A\right)^{2/3}\times10^{-8}$$

$$= \left(\frac{10.5\times6.022\times10^{23}}{108}\right)^{2/3}\times10^{-8}$$

$$= 1.50\times10^7$$

∴ $x = 7$

2. (8) : There are 4Na^+ ion and 4Cl^- ions per unit cell. Total Na^+ and Cl^- ions are 8.

3. (4) : It corresponds to fcc unit cell. Therefore, the number of atoms present per unit cell is 4.

4. (6) : Since radius ratio lies between 0.414 – 0.732, its coordination number is 6.

5. (7) : Suppose number of atoms N in *hcp* lattice = n

No. of tetrahedral voids = $2n$

$$\text{No. of M atoms} = \frac{2}{3}\times2n = \frac{4n}{3}$$

$$\text{Formula} = M_{\frac{4n}{3}}N_n \text{ or } M_{\frac{4}{3}}N_1 \text{ or } M_4N_3.$$

Total number of M and N atoms = 7.

6. (6) : In one *hcp* unit cell, there are 6 atoms.

No. of octahedral voids = 6

No. of tetrahedral voids = 12

Difference = 12 – 6 = 6.

7. (1) : Coordination no. in *ccp* = 12

Coordination no. in *hcp* = 12

Ratio = 12/12 = 1.

8. (5) : Suppose the atoms Y in *ccp* = n

No. of tetrahedral voids = $2n$

No. of X atoms = $2n/3$

Formul $X_{2/3n}Y_n$ or X_2Y_3

∴ $a + b = 5$

9. (5) : Contribution of atoms on the corners = $8\times\frac{1}{8} = 1$.

Since atoms on the body diagonal are not shared by any other unit cell and there are four body diagonals, their contribution per unit cell = 4

∴ Total number of atoms in the unit cell = 4 + 1 = 5.

10. (8) : A truncated octahedron has 14 faces (8 regular hexagons and 6 squares), 36 edges and 24 vertices.

11. (2) : Volume of unit cell = $(400\times10^{-10})^3$ cm^3

Mass of element = 256 g

Density of element = 8 g cm^{-3}

$$\text{Volume of 256 g of element} = \frac{256}{8} = 32\text{ cm}^3$$

$$\text{No. of unit cells} = \frac{32}{(400\times10^{-10})^3} = 5\times10^{23}\text{ unit cells}$$

Since the structure is *fcc*, number of atoms present in a unit cell = 4

No. of atoms in 256 g = $5\times10^{23}\times4$

$$= \mathbf{2\times10^{24}\ atoms}$$

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12. (3.00) : MX having NaCl structure

No. of M^+ ions = 4 No. of X^- ions = 4

For structure Z constructed from MX

(*i*) After removing all X^- ions except the centred one,

No. of M^+ ions = 4 No. of X^- ions = 1

(*ii*) No. of face centred M^+ ions removed = $6\times\frac{1}{2}=3$

No. of M^+ ions replaced by X^- ions = 3

$\therefore$ No. of M^+ ions left = 1 No. of X^- ions = 1 + 3 = 4

(*iii*) No. of corners M^+ ions $=8\times\frac{1}{8}=1$.

No. of M^+ ions left =1–1=0 No. of X^- ions = 4

(*iv*) Replacing central X^- by M^+

No. of M^+ ions = 0+1=1 No. of X^- ions =4–1=3

$$\frac{\text{No. of } X^- \text{ ions}}{\text{No. of } M^+ \text{ ions}}=\frac{3}{1}=3.00$$

NCERT Exemplar Problems : MCQs Type-I

2. (*b*) : Crystalline solids are not isotropic in nature. These are anisotropic in nature.

4. (*d*) : In antiferromagnetism, the magnetic moments are in a compensatory way so as to give zero net magnetic moment because of cancellation of individual magnetic moments.

5. (*a*) : Quartz glass is amorphous and therefore, refractive index is same in all directions.

12. (*b*) : Graphite is a good conductor of electricity due to the presence of free (π) electrons.

14. (*d*) : CrO_2 show electrical behaviour as metals.

19. (*b*) : The overall charge is neutral.

20. (*d*) : *n*-type of semiconductor is formed when silicon is doped with atoms having more than four electrons (*e.g.* P, As).

21. (*b*) : A *fcc* unit cell has 4 atoms per unit cell and each atom has two tetrahedral sites. Therefore, the number of tetrahedral sites in *fcc* unit cell is eight.

22. (*a*) : AgBr shows both Schottky defect and Frenkel defect.

23. (*b*) : *hcp* and *ccp* occupy 74% of the available space and have most efficient packing.

25. (*d*) : It has AB AB AB type of arrangement and therefore, fourth layer is not aligned with particles of first layer.

26. (*a*), (*d*) : In NaCl, both Na^+ and Cl^- ions have six C.N. (*d*) is also correct. The C.N. of both Zn^{2+} and S^{2-} ions are four.

28. (*d*) : Electronic defects are introduced by doping.

30. (*b*): In ferromagnetic substances ordering of magnetic moments may persist even when magnetic field is removed. Therefore, these can be magnetised permanently.

31. (*d*) : Opposite to the direction of magnetic field.

33. (*b*) : *fcc* (74%) > *bcc* (68%) > Simple cubic (52.4%)

34. (*a*): because cations are dislocated to interstitial sites.

35. (*d*) : In *ccp*, there are four atoms per unit cell and therefore eight tetrahedral voids.

36. (*a*) : In *fcc*; $a=\frac{4r}{\sqrt{2}}$ or $2\sqrt{2}r$; in *bcc* $a=\frac{4r}{\sqrt{3}}$ and in cubic, $a = 2r$.

37. (*a*): The conductivity of metals is much more than that of insulators but the conductivity of semiconductors is less than metals and more than insulators.

NCERT Exemplar Problems : MCQs Type-II

40. (*c, d*) : (*c*) is not true because impurity defect changes the mass but not the volume and therefore, density changes.

(*d*) Frenkel defect neither changes mass nor volume.

42. (*a, b*) : (*c*) is wrong because electrons move towards anode and holes move towards cathode.

(*d*) is also not true.

43. (*b, c*) : (*a*) is false because silicon doped with electron rich impurity is *n*-type semiconductor.

(*d*) is false because conductivity of *n*-type semiconductor increases due to extra electrons and not due to vacancy.

45. (*b, c*) : In NaCl, Cl^- ions have fcc arrangement and number of Cl^- ions per unit cell = 4. Number of tetrahedral voids will be 4 × 2 = 8.

Tetrahedral voids are double the number of octahedral voids.

47. (*a, c*) : Impurities of As and P when doped to silicon give *n*-type semiconductor.

50. (*a, b, c*) : SiC, AlN and diamond are covalent network solids.

53. (*b, d*) : Vacancy defect and Schottky defect decrease the density.

NCERT Exemplar Problems : Assertion Reason Type Questions

59. (*a*) : Simple cubic unit cell has one atom because there are 8 atoms at the corners, each contributing 1/8.

60. (*b*) : Graphite is a good conductor of electricity because of the presence of π electrons.

61. (*c*) : Reason is not correct though assertion is correct.

62. (*b*) : Both assertion and reason statements are correct but reason is not correct explanation for the assertion.

63. (*c*) : Assertion is correct but the reason is not the correct explanation of assertion. This is because intermediate conductivity of semiconductors is due to small energy gap between filled valence band and empty conduction band.

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Unit Practice Test

for Board Examination

Time Allowed : 1 Hr. Maximum Marks : 25

1. What is the maximum coordination number of an atom in a *hcp* crystal structure of an element? (1)
2. Both diamond and rhombic sulphur are covalent solids but the latter has very low melting point than the former. Why? (1)
3. Why is Frenkel defect not found in pure alkali metal halides? (1)
4. A group 14 element is to be converted into *n*-type semiconductor by doping with a suitable impurity. To which group should this impurity belong? (1)
5. How do the structures of quartz and quartz glass differ from each other. (1)
6. Analysis of a metal oxide shows its empirical formula $M_{0.96}O_{1.0}$. Calculate the percentage of M^{2+} and M^{3+} ions in the crystal. (2)
7. What are Schottky and Frenkel defects? How does density of a solid get affected by these defects? (2)
8. Ferric oxide crystallizes in a hexagonal close packed array of oxide ions with two out of every three octahedral voids occupied by ferric ions. Derive the formula of the ferric oxide. (2)
9. An element crystallizes in a body centred cubic structure with a cell edge of 288 pm. The density of the element is 7.2 g cm^{-3}. How many atoms are present in 208 g of the element ? (3)
10. Explain
    (*i*) Some of the very old glass objects appear slightly milky instead of being transparent.
    (*ii*) Zinc oxide exhibits enhanced electrical conductivity on heating.
    (*iii*) $CdCl_2$ will induce Schottky defect if added to silver chloride crystal. (3)
11. Explain the following terms with suitable examples :
    (*i*) Ferrimagnetism
    (*ii*) Intrinsic conduction of solids
    (*iii*) Ferromagnetism. (3)
12. (*a*) If the radius of octahedral void is r and the radius of the atoms in the close packing is R, derive a relationship between r and R.
    (*b*) What is a semiconductor ? Describe the two main types of semiconductors and contrast conduction mechanism in them. (5)

▶ To check your performance, see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part I of the book.

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UNIT 6

THERMODYNAMICS

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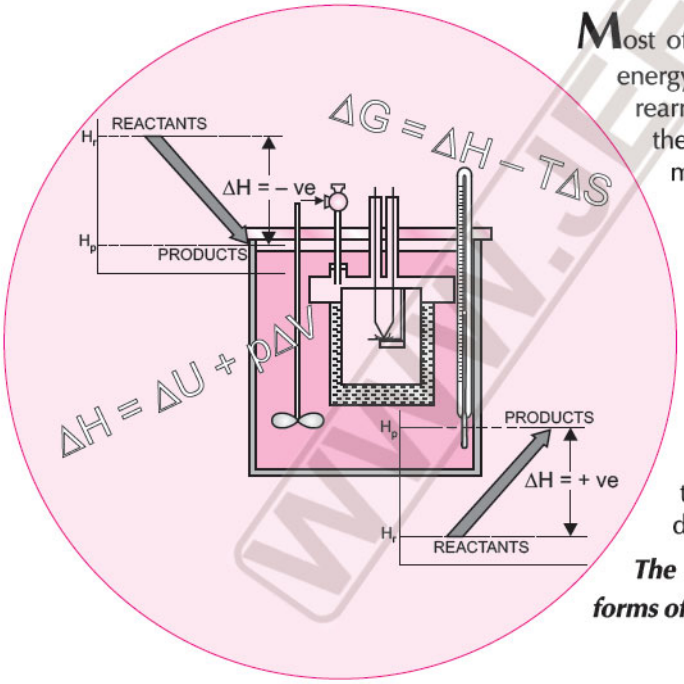

Most of the physical and chemical changes are accompanied by energy changes. These energy changes take place because of the rearrangement of atoms in reactants to form products. Sometimes, the energy changes associated with the chemical reactions are more significant than the products of the reaction *e.g.,* burning of fuel, coal or natural gas. These processes satisfy our energy needs. The most common form in which the energy appears is **heat**. There are other forms of energy also such as light, work, electrical energy, chemical energy and nuclear energy. These different forms of energy may be transformed from one into the other. For example, heat can be converted into mechanical energy to operate a machine or propel a vehicle. The chemical energy may also be converted into electrical energy through a galvanic cell like dry cell. The transformation of heat into work is achieved with the help of devices called **engines.**

The branch of science which deals with the study of different forms of energy and their interconversion is called thermodynamics.

There are three main laws of thermodynamics. The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. These laws apply only when a system is in equilibrium or move from one equilibrium state to another equilibrium state.

SOME BASIC TERMS AND CONCEPTS

Let us learn some terms which are commonly used in the discussion of thermodynamics.

System and Surroundings

System. *A specified part of the universe which is under observation* is called the **system.**

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A system is called ***heterogeneous*** if physical properties and chemical composition are identical throughout the system. On the other hand, a system is said to be ***heterogeneous*** if it consists of parts (or phases) each of which has different physical and chemical properties. Thus,

a homogeneous system consists of one phase while a heterogeneous system consists of two or more phases.

Surroundings. *The remaining portion of the universe which is not a part of the system* is called the **surroundings.** In other words, surroundings include everything other than the system. The system and the surroundings together constitute the universe.

System + Surroundings = Universe

However, it may be noted that the entire universe is not affected by the changes taking place in the system. Therefore, for all practical purposes the surroundings are that portion of the remaining universe which can interact with the system. Generally, the region of space in the neighbourhood of the system is taken as surroundings.

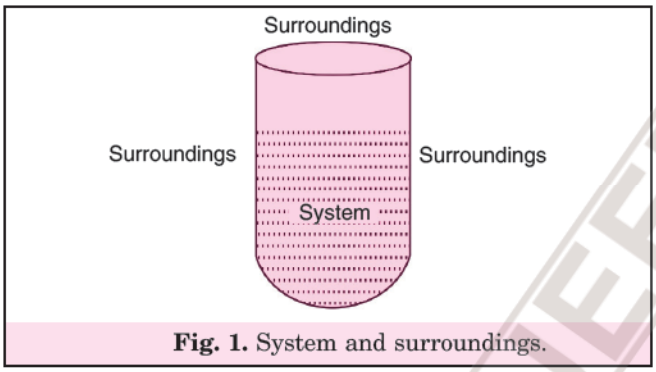

Fig. 1. System and surroundings.

The system and the surroundings are separated by real or imaginary boundaries. The boundary also defines the limits of the system. The system and the surroundings can interact across the boundary.

For example, if we wish to investigate the behaviour of alcohol in water, we take alcohol in a beaker and add water to it. Here, the contents of the beaker constitute the system, beaker serves as boundary and everything else is the surroundings. The surroundings can affect the system by the transfer of matter or energy.

Types of Systems :

Systems may be classified into three types depending upon the movement of matter and energy in or out of the system.

(*i*) **Open system**

A system which can exchange matter as well as energy with the surroundings is called an **open system.** For example, hot coffee in an open flask is an example of open system because it can gain or lose matter as well as energy. Similarly, if we carry out a reaction between zinc granules and hydrochloric acid in an open beaker, it constitutes an open system because hydrogen evolved during the reaction (mass) goes out from the system to the surroundings and at the same time heat evolved during the reaction escapes from the system to the surroundings.

(*ii*) **Closed system**

A system which can exchange energy but not matter with its surroundings is called a **closed system.** Hot coffee in a stainless flask is an example of closed system because energy can be gained or lost (through the steel walls) but not matter. Similarly, all chemical reactions carried out in closed containers are the examples of closed system. For example, heating of hydrogen iodide in a sealed glass bulb constitutes a closed system because there is exchange of heat energy from surroundings to the system but no exchange of matter takes place.

(*iii*) **Isolated system**

A system which can neither exchange matter nor energy with the surroundings is called an **isolated system.** There is no perfectly isolated system. However, a system which is completely sealed to prevent inflow or outflow of matter and is thermally insulated to prevent flow of heat can be considered as an isolated system. For example, hot coffee in a corked thermos flask is an example of isolated system, because it can neither gain or lose energy nor gain or lose matter. Similarly, all chemical reactions carried out in closed containers insulated from the surroundings are the examples of isolated system.

These three types of systems for the vaporisation of a liquid are shown in Fig. 2 and the exchange of matter and energy between the system and the surroundings is summarized in Fig. 3

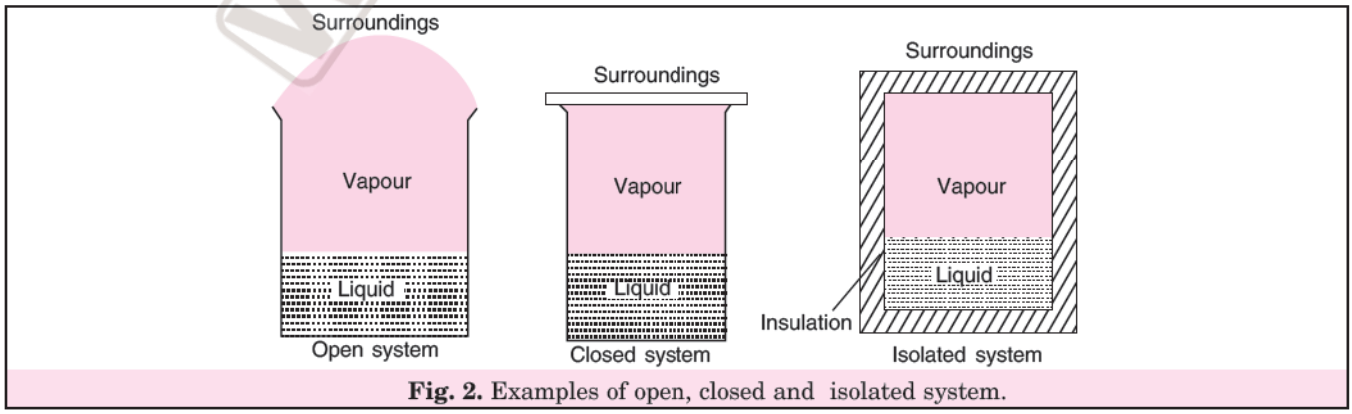

Fig. 2. Examples of open, closed and isolated system.

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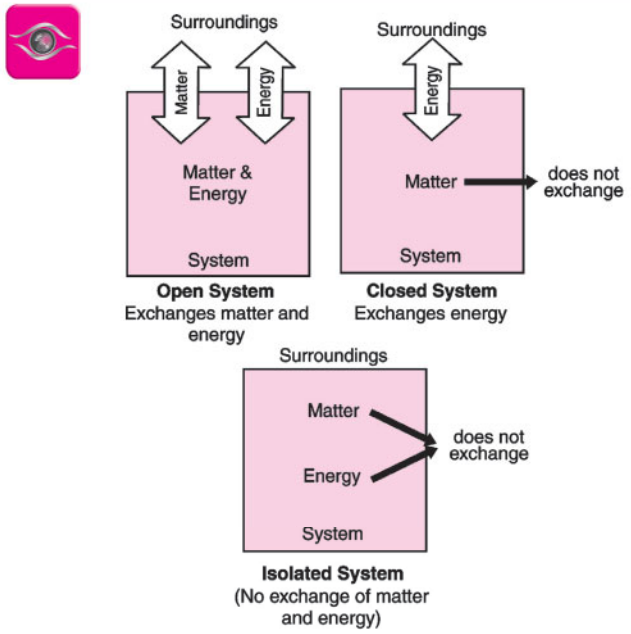


Fig. 3. Illustration of exchange of matter and energy with surroundings in open, closed and isolated system.

All physical and chemical processes taking place in open in our daily life are open systems because these are continuously exchanging matter and energy with the surroundings.

Macroscopic Properties of the System

Thermodynamics deals with matter in terms of bulk (large number of chemical species i.e. atoms, molecules or ions) behaviour. *The properties of the system which arise from the bulk behaviour of matter* are called **macroscopic properties**. The common examples of macroscopic properties are pressure, volume, temperature, surface tension, viscosity, density, refractive index, etc.

In thermodynamics, the macroscopic properties can be sub-divided into two types :

(*i*) Extensive properties and

(*ii*) Intensive properties,

Extensive and Intensive Properties

(*i*) **Extensive properties.** *The properties of the system whose value depends upon the amount of substance present in the system* are called **extensive properties.** For example, mass, volume, surface area, internal energy, enthalpy, entropy, free energy, heat capacity, etc.

(*ii*) **Intensive properties.** *The properties of the system whose value is independent of the amount of substance present in the system* are called **intensive properties.** These properties depend only upon the nature of the substance. For example, temperature, pressure, viscosity, surface tension, dielectric constant, specific heat capacity, vapour pressure, refractive index, etc.

It may be noted that an extensive property may become intensive property by specifying unit amount of the substance. For example, mass and volume are extensive properties but density (mass per unit volume) and specific volume (volume per unit mass) are intensive properties. In general, the ratio of two extensive properties is always intensive *i.e.*,

$$\frac{\text{Extensive property}}{\text{Extensive property}} = \text{Intensive property}$$

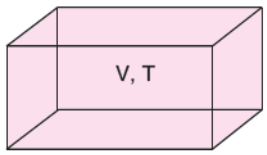
e.g., $\dfrac{\text{Moles of a component (extensive)}}{\text{Total moles (extensive)}}$ = Mole fraction (intensive).

Thus molar property (χ_m) is the value of an extensive property χ of the system for one mole of the substance. If n is the amount of matter, then $\chi_m = \dfrac{\chi}{n}$ is independent of the amount of matter and hence is intensive property. Thus, **molar property is intensive property**. For example, molar volume, molar heat capacity.

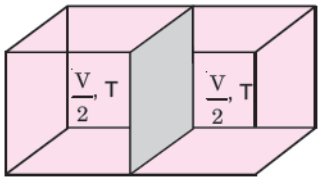
It may be noted that **force** is an **extensive property** but **pressure** is an **intensive property** because it is the force exerted per unit area.

To understand the distinction between extensive and intensive properties, consider a gas enclosed in a cantainer of volume V at temperature T, as shown in Fig. 4. Let us make a partition such that volume is halved. Now, each part will have volume ½ V (*i.e.* V/2) but the temperature will remain the same. This shows that volume is an extensive property and temperature is an intensive property.

It may be noted that extensive properties are additive but intensive properties are not.



(*a*) A gas at volume V and temperature T



(*b*) Partition: each part having half the volume of the gas $\left(\dfrac{V}{2}\right)$.

Fig. 4.

State of a System and State Variables

The state of a system means *the condition of existence of the system when its macroscopic properties have definite values*. If any of the macroscopic properties of the system changes, the state of the system is also said to change. Thus, the state of the system is fixed by its macroscopic properties.

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State Variables

The measurable properties required to describe the state of the system are called **state variables.** For example, temperature, pressure, volume, composition, etc. are the state variables. It may be noted that for describing a system, it is not necessary to specify the values of all state variables. For any system, a certain minimum number of variables is sufficient to define its state because the other variables become automatically fixed and have definite values. For example, consider a system consisting of an ideal gas. The state of this system may be defined by only three variables such as temperature (T), pressure (p) and volume (V). The values of other variables (such as amount of gas, density, etc.) will be definite and can be easily calculated.

State Functions

A **state function** *is a property of the system whose value depends only upon the state of the system and is independent of the path or manner by which the state is reached.* The change in the value of these properties (state functions) depends only upon the initial and final states of the system and not on the path by which the change from initial to final state is brought about. Some common state functions are pressure (p), volume (V), temperature (T), internal energy (U), enthalpy (H), entropy (S), etc.

Thermodynamic equilibrium

A system is said to be in ***thermodynamic equilibrium*** *if its macroscopic properties (like temperature, pressure, etc.) do not change with time.* The **initial state** of the system corresponds to the starting state of the system in equilibrium before any type of interaction with the surroundings. In the **final state,** the system attains equilibrium after interaction with the surroundings. The state function gives the difference in the property of the initial state and the final state. The interaction with the surroundings means the transfer of matter or energy or both.

Types of Processes

The state of a thermodynamic system can be changed by a process. In other words, a **process** *gives the path or operation by which a system changes from one state to another*. The process may be accompanied by an exchange of matter and energy between the system and the surroundings. This results in change in at least one of the state variables of the system. There are certain processes in which a particular state variable (thermodynamic property of the system) is kept constant. These are identified with special names. Some common types of processes are :

(*i*) **Isothermal process.** *A process in which the temperature of the system remains constant.* In such a system, heat is either supplied to the system or removed from it.

(*ii*) **Adiabatic process.** *A process in which the system does not exchange heat with the surroundings, i.e., no heat leaves or enters the system.* In such a process, temperature of the system always changes. The systems in which such processes occur are thermally insulated from the surroundings.

(*iii*) **Isobaric process.** *A process in which the pressure of the system remains constant.*

(*iv*) **Isochoric process.** *A process in which the volume of the system remains constant.*

(*v*) **Cyclic process.** *A process in which the system undergoes a series of changes and ultimately returns to its original state* is called a **cyclic process**

(*vi*) **Reversible process.** *A process in which the direction may be reversed at any stage by merely a small change in a variable like temperature, pressure, etc.*

To understand a reversible process, consider a gas enclosed in a frictionless movable piston. Suppose the external pressure p_{ex} on the outer surface of the piston is set equal to the pressure, p of the gas. Under these conditions, the piston does not move at all and the system is said to be in a state of equilibrium. Now, suppose the external pressure p_{ex} is reduced by an infinitesimally small amount. Because p_{ex} is infinitesimally smaller than p, the piston moves out slowly and the gas expands. However, if p_{ex} is slightly increased so that it becomes infinitesimally greater than p, the gas gets compressed and the piston moves inwards.

Thus, the necessary condition for reversible expansion is : $p_{ext} = p_{int} - dp$

For reversible compression, $p_{ext} = p_{int} + dp$

Hence, in general for a reversible process:

$p_{ext} = p_{int} \pm dp$

Thus, in a reversible process, the driving force is only infinitesimally greater than the opposing force and is carried our infinitesimally showly. In this process, at every instant, the system remains virtually in a state of equilibrium with the surroundings.

(*vii*) **Irreversible process.** *A process which is not reversible* is called an **irreversible process**. The driving force is very different than the opposing force.

Differences between Reversible and Irreversible Processes.

Reversible process	*Irreversible process*
1. The process in which the direction may be reversed at any stage by merely a small change in a variable like temperature, pressure, etc.	1. A process in which the direction cannot be reversed at any stage by change in a variable like temperature, pressure, etc.
2. In a reversible process, the driving force is only infinitesimally greater than the opposing force at all stages.	2. The driving force is different than the opposing force.
3. It is carried out infinitesimally slowly.	3. It is carried out rapidly.
4. At any stage during the process, equilibrium is not disturbed.	4. Equilibrium may exist only after the completion of the process.
5. It is only imaginary and cannot be achieved in actual process.	5. All natural processes are irreversible.
6. Work obtained in this process is maximum.	6. Work obtained in this process is not the maximum.

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All natural processes are irreversible.

SOLVED EXAMPLES

Example 1.

Classify the following as open, closed or isolated systems :

(i) A beaker containing boiling water.

(ii) A chemical reaction taking place in an enclosed flask.

(iii) A cup of tea placed on a table.

(iv) Hot water placed in perfectly insulated closed container.

(v) A thermos flask containing hot coffee.

Solution : Types of system :

(*i*) Open system (*ii*) Closed system (*iii*) Open system (*iv*) Isolated system (*v*)Isolated system.

INTERNAL ENERGY AND INTERNAL ENERGY CHANGE

Every substance possesses a definite quantity of energy which depends upon factors such as chemical nature of the substance, temperature and pressure. This is known as **intrinsic energy** or **internal energy** and is represented by the symbol U (earlier it was represented by the symbol E). It is made up of kinetic energy and potential energy of the constituent particles. The kinetic energy arises due to motion of its particles and includes their translational energy, rotational energy, vibrational energy etc. The potential energy arises from different types of interactions between the particles and includes *electronic energy, nuclear energy, energy due to molecular interactions,* etc.

The sum of all forms of energies stored within a substance (or a system) is called **its internal energy.**

Internal Energy Change as a State Function

Although every substance or a system has a definite amount of internal energy but the absolute value of internal energy possessed by a substance cannot be calculated. This is because it is not possible to find the accurate values of different types of energies, stored in a system. However, we are interested mostly in change in internal energy which occurs during chemical reactions. The change in internal energy of a reaction may be considered as the difference between the internal energies of the two states.

Let U_A and U_B are the internal energies in states A and B respectively. Then the difference between the internal energies in the two states will be

$$\Delta U = U_B - U_A$$

The difference in internal energies (ΔU) has a fixed value and will be independent of the path taken between two states A and B. For chemical reactions, the change in internal energy may be considered as the difference between the internal energies of the products and that of the reactants, *i.e.*,

$$\Delta U = U_{products} - U_{reactants} = U_p - U_r$$

where U_p is the internal energy of the products, U_r is internal energy of the reactants and ΔU gives the change in internal energy.

If the internal energy of the products is **less** than the internal energy of the reactants, then ΔU would be **negative.**

$$\Delta U = U_p - U_r = -\text{ve} \qquad (\because U_p < U_r)$$

On the other hand, if the internal energy of the products is **more** than the internal energy of the reactants, the ΔU would be **positive.**

$$\Delta U = U_p - U_r = +\text{ve} \qquad (\because U_p > U_r)$$

Thus, the internal energy, U is a *state function.* This means that ΔU depends only on the initial and final states and is independent of the path. In other words, ΔU will be same even if the change is brought about differently.

MODES OF TRANSFERENCE OF ENERGY BETWEEN SYSTEM AND SURROUNDINGS

Every system has a definite amount of energy. It can exchange energy (lose or gain) with the surroundings in a variety of ways. The two important modes of transference of energy between the system and the surroundings are heat and work as

- Heat passes into or out of the system
- Work is done on or by the system.

1. Heat (q)

Energy is exchanged between the system and the surroundings as heat if they are at different temperatures. For example, if a system is at a higher temperature than the surroundings, then energy (or heat) is lost to the surroundings causing a fall in temperature of the system and rise in temperature of the surroundings [Fig. 5 (*a*)]. This process continues till the temperatures of the system and the surroundings become equal. On the other hand, if the temperature of the system is lower than that of the surroundings, then energy is gained by the system [Fig. 5 (*b*)]. In other words, we say that there is a flow of heat from system to surroundings if system has higher temperature and there is flow of heat from surroundings to the system if the former is at higher temperature.

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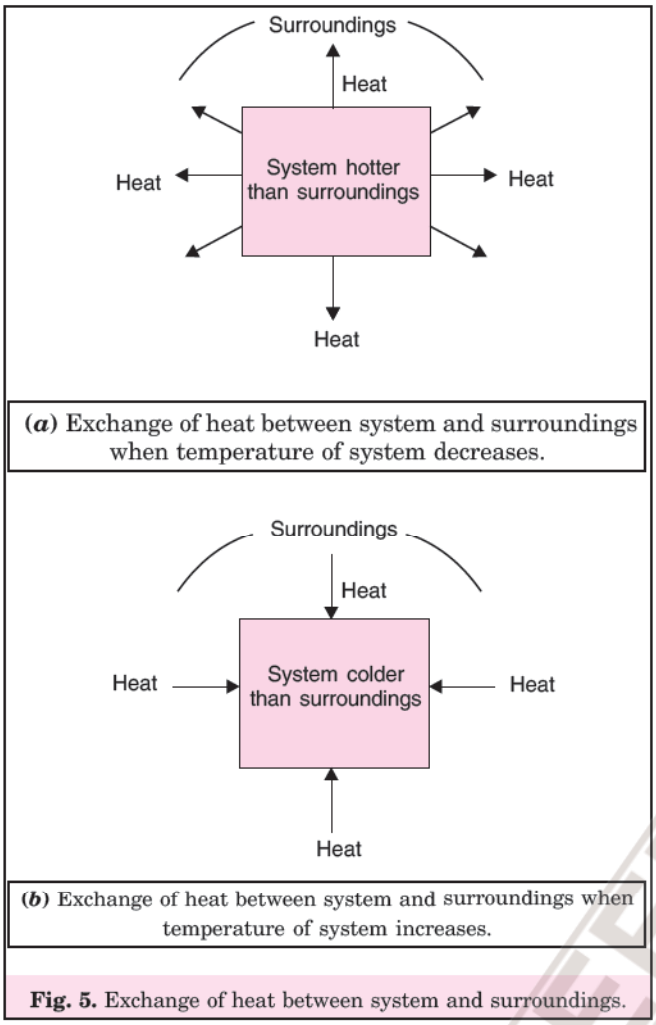

(*a*) Exchange of heat between system and surroundings when temperature of system decreases.

(*b*) Exchange of heat between system and surroundings when temperature of system increases.

Fig. 5. Exchange of heat between system and surroundings.

This *exchange of energy which is a result of temperature difference is called* **heat, *q*.** For example, suppose we take water at a temperature T_A in a container having thermally conducting walls (say made up of copper) and enclose it in a huge heat reservoir at temperature, T_B. The system will absorb heat from the reservoir and this heat absorbed by the system can be measured in terms of temperature difference, $T_B - T_A$.

In this case, change in internal energy will be

$$\Delta U = q$$

when no work is done at constant volume. Obviously,

⇒ ***q* is positive when heat is transferred from the surroundings to the system and**

⇒ ***q* is negative when heat is transferred from system to the surroundings.**

2. Work (w)

It is another mode of transference of energy. Work is said to be performed *if the point of application of force is displaced in the direction of the force.* It is equal to the force multiplied by the displacement (distance through which the force acts). If f is the force and dl is the displacement of the point of application in the direction in which force acts, then work done is given by

$$w = f \times dl$$

There are two main types of work which we generally come across. These are (*i*) electrical work, and (*ii*) mechanical work. Electrical work is important in systems where reaction takes place between ions whereas mechanical work is performed when a system changes its volume in the presence of external pressure. Mechanical work is important specially in systems that contain gases. This is also known as *pressure-volume work.*

Let us examine a change in internal energy by doing work. Let us consider a system containing some quantity of water in a thermos flask or in an insulated beaker. This would not allow exchange of heat between the system and the surroundings through its boundary. We call this type of system as **adiabatic system**. The manner in which the state of such a system may be changed will be called **adiabatic process** because there is no transfer of heat between the system and the surroundings. In this system, the boundary wall which separates the system and the surroundings is also called **adiabatic wall.**

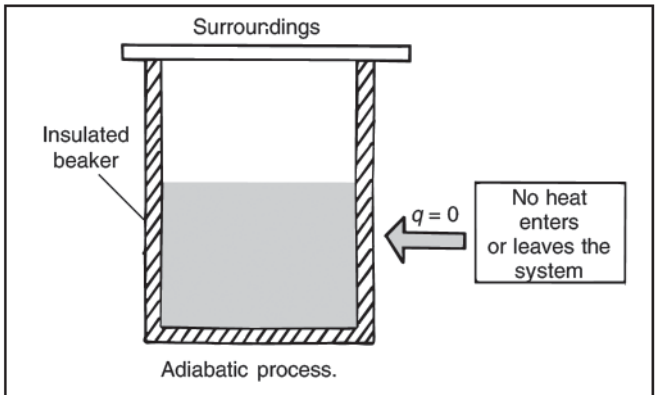

Fig. 6. Adiabatic process.

Let us bring the change in internal energy by doing some work on the system. Let the initial state of the system be state A and its temperature be T_A. Let the internal energy of the system in state A be U_A. We can change the state of the system in two different ways :

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1. One way. Suppose we do some mechanical work (say 1 kJ) by rotating a set of small paddles and thereby churning the water. This will convert all the mechanical energy of the rotating paddle into heat energy by friction between paddles and water. This heat energy will result into rise of temperature. Let the next state be called state B and its temperature be T_B ($T_B > T_A$). Let the internal energy of the system in state B be U_B and change in internal energy $\Delta U = U_B - U_A$.

2. Second way. Suppose we do an equal amount of electrical work (1 kJ). We heat the water with the help of immersion rod. It will be observed that change in temperature is same as in earlier case i.e., $T_B - T_A$.

In fact J.P. Joule performed a series of experiments in 1840–1850 to find the relation between mechanical work and heat produced. By performing careful experiments, Joule found that a given amount of work done on the system, no matter how it was done (irrespective of the path), always produced the same change of state as measured by the change in the temperature of the system. For example, irrespective of the method used for converting mechanical energy to heat, every time for 4.186 kJ of mechanical work (or work done) exactly same amount of heat was produced which could raise the temperature of 1 kilogram of water by 1°C.

Thus, we observe that the value of internal energy is characteristic of the state of a system and the adiabatic process (w_{ad}) required to bring about a change is equal to the difference between the value of U in one state and that in another state, ΔU i.e.,

$$\Delta U = \Delta_{final} - U_{initial} = w_{ad}$$

Thus, **internal energy U of the system is a state function. The positive sign expresses that w_{ad} is positive, when work is done on the system. Similarly, if the work is done by the system, w_{ad} is negative.**

Pressure-Volume Work

It is the work done when the gas expands or contracts against the external pressure (usually atmospheric pressure). To understand this, consider a cylinder fitted with a frictionless and weightless piston having area of cross-section equal to A. Let it contains a mole of a gas of volume V_i and the pressure of the gas inside is p [Fig.7(a)]. Let the external pressure acting on the piston is p_{ex}. If the external pressure p_{ex} is slightly greater than p (*i.e.*, $p_{ex} > p$), piston is moved downward till the pressure inside the cylinder becomes equal to p_{ex} as shown in Fig. 7 (*b*). Let this change be achieved in a single step and the final volume be V_f.During the compression, suppose the piston moves a very small distance l. Then change in volume is given by

Volume change = $l \times A$

or $\Delta V = V_f - V_i = l \times A$

We know that Pressure $= \dfrac{\text{Force}}{\text{Area}}$

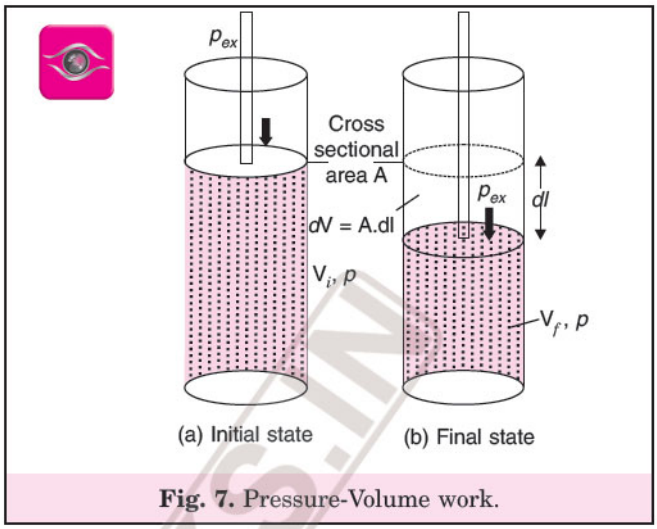

Fig. 7. Pressure-Volume work.

or Force = Pressure × Area

Therefore, force on the piston

$$f = p_{ex} \cdot A$$

If w is the work done on the system by movement of the piston, then

$$\text{work, } w = \text{force} \times \text{distance}$$
$$= p_{ex} \cdot A \cdot l$$
$$= p_{ex}(-\Delta V)$$
$$\text{or} \quad = -p_{ex}\Delta V \quad \ldots(i)$$
$$= -p_{ex}(V_f - V_i)$$

It may be noted that the negative sign of this expression is necessary to give the conventional sign for w. It is positive for compression as work is done on the system. Here, $(V_f - V_i)$ will be negative so that negative multiplied by negative will be positive.

However, if the external pressure is slightly less than the pressure of the gas (*i.e.*, $p_{ex} < p$), the gas will expand *i.e.*, the work will be done by the system on the surroundings. In that case, V_f will be more than V_i and ΔV will be positive and therefore, w will be negative as per convention, *i.e.*

$$w = -p_{ex}\Delta V = \textbf{–ve}$$

Obviously, if there is no change in volume, *i.e.*, $\Delta V = 0$, no work is done by the system, *i.e.*, work = 0.

Alternatively, if the system is at lower pressure, piston will be pushed down until the pressure of the system becomes equal to that of the surroundings. In this case, *work is done on the system by the surroundings.* In this way, energy transfer takes place from the system to the surroundings as work. If the system loses energy, we say that the *work is done by the system.* Alternatively, if the system gains energy, we say that *work is done on the system.*

Thus,

(*i*) *If the gas expands,* $V_f > V_i$ and work is done by the system and ***w* is negative.**

(*ii*) *If the gas contracts,* $V_f < V_i$ and work is done on the system and ***w* is positive.**

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Now, let us suppose that pressure is not constant at every stage of compression, but changes in a number of finite steps. Then work done on the gas will be summed over all the steps and will be equal to

$$w = -\sum p_{ex}\,\Delta V$$

This is shown in Fig. 8(*a*).

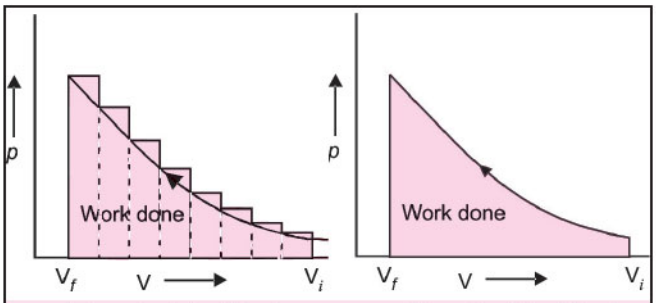

Fig. 8. *(a)* pV–plot, when pressure is not constant and changes in finite steps during compression from initial volume (V_i) to final volume (V_f). Work done on the gas is represented by the shaded area.

Fig. 8. *(b)* pV–plot, when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume (V_i) to final volume (V_f). Work done on the gas is represented by the shaded area.

If the pressure is not constant but changes in an infinite number of steps such that it is always infinitesimally greater than the pressure of the gas (reversible conditions). Let at each stage the piston moves an infinitesimally small distance *dl*. Then the infinitesimally small decrease in volume is dV as

$$dV = A.dl$$

We know that pressure $= \dfrac{\text{force}}{\text{area}}$

or force = pressure × area

Therefore, force on the piston,

$$f = p_{ex} \cdot A$$

If the small work done on the system by the movement of the piston is *dw*, then

Work = Force × Distance

$$dw = p_{ex}.\,A.\,dl$$

But A × *dl* = *d*V is a small change in volume of the gas so that

$$dw = p_{ex} \cdot dV$$

If the volume of the system changes by a finite quantity from volume V_i to V_f, then total work done on the system, *w* can be obtained by integrating p_{ex}. *d*V (when *p* is constant) over the volume change from V_i to V_f. Thus,

$$w = -\int_{V_i}^{V_f} p_{ex}.dV \qquad ...(ii)$$

$$= -p_{ex}(V_f - V_i)$$

$$= -p_{ex}\,\Delta V \qquad ...(iii)$$

It may be noted that in the above expression, p_{ex} at each stage is equal to $(p_{in} + dp)$ in case of compression [Fig. 8 (*b*)]. Similarly, in an expansion process under similar conditions, the external pressure is always less than the pressure of the system i.e., p_{ex} $= (p_{in} - dp)$. So in general case, we may write $p_{ex} = (p_{in} \pm dp)$. Such processes are called reversible processes. Thus,

a process or change is said to be reversible, if it is brought out in such a way that the process could at any moment be reversed by an infinitesimal change. A reversible process proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other.

The processes which are not reversible are called irreversible processes.

It may noted that we can also relate work to internal pressure of the system under reversible conditions if volume changes from V_1 to V_2. It may be expressed as

$$w_{rev} = -\int_{V_1}^{V_2} p_{in}\,dV \qquad ...(iv)$$

This may be obtained from Eq. (*ii*) as

$$w_{rev} = -\int_{V_1}^{V_2} p_{ex}\,dV = -\int_{V_1}^{V_2} (p_{in} \pm dp)\ \text{dV}$$

$$= -\int_{V_1}^{V_2} (p_{in}\,dV \pm dp\,.\,dV)$$

(*dp* and *d*V are infinitesimally small so that *dp*.*d*V is doubly infinitesimal and can be neglected).

$$w_{rev} = -\int_{V_1}^{V_2} p_{in.}\,dV \qquad ...(v)$$

Now pressure of the gas (p_{in} which we may write as p) can be expressed in terms of its volume through gas equation

$$pV = nRT$$

or $$p = \frac{nRT}{V}$$

Therefore, at constant temperature (i.e., for isothermal process)

$$w_{rev} = -\int_{V_1}^{V_2} nRT\,\frac{dV}{V} = -nRT\,ln\,\frac{V_2}{V_1}$$

or $$\boldsymbol{w_{rev} = -2.303nRT\log\frac{V_2}{V_1}} \quad \textbf{... (vi)}$$

At constant temperature,

$$p_1V_1 = p_2V_2 \text{ or } \frac{V_2}{V_1} = \frac{p_1}{p_2}$$

so that

$$\boldsymbol{w_{rev} = -2.303nRT\log\frac{p_1}{p_2}}$$

Free expansion. Expansion of a gas in vacuum ($p_{ex} = 0$) is called **free expansion**. It may be noted that no work is done during free expansion of an ideal gas whether the process is reversible or irreversible.

In addition to these two modes, *radiant energy* and

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electrical energy are also modes of transference of energy between the system and the surroundings.

Units of Heat and Work

The heat changes are measured in **calories** (cal), kilocalories (kcal), joules (J) or kilojoules (kJ). These are related as :

$$1 \text{ cal} = 4.184 \text{ J}$$
$$1 \text{ kcal} = 4.184 \text{ kJ}$$

The S.I. unit of heat is joule or kilojoule

Work is measured in terms of ergs or joules.

$$1 \text{ Joule} = 10^7 \text{ ergs.}$$

The S.I. unit of work is joule.

and $1 \text{ J} = 1 \text{ Nm} = 1 \text{kg m}^2\text{s}^{-2}$.

These can easily be obtained as :

Work = Force × Distance = N × m = Nm = 1J

Force = mass × acceleration

$\therefore$ Work = $\text{kg} \times \text{ms}^{-2} \times \text{m} = \text{kg m}^2\text{s}^{-2}$

Thus, **1J = 1 kg m^{2}s^{-2}**

Practice Problems

1. Which of the following are open, close or nearly isolated systems ?

(*i*) Human being (*ii*) the earth (*iii*) can of tomato soup (*iv*) Ice cube tray filled with water (*v*) A satelite in an orbit (*vi*) Coffee in a thermos flask and (*vii*) Helium filled in balloon. ***N.C.E.R.T.***

2. Which of the following are state functions ?

(*i*) height of a hill

(*ii*) distance travelled in climbing the hill

(*iii*) energy change in climbing the hill

Answers to Practice Problems

1. (*i*) open (*ii*) open (*iii*) close (*iv*) open (*v*) open (*vi*) isolated (*vii*) close.

2. (*i*) and (*iii*).

LAW OF CONSERVATION OF ENERGY : FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is also known as **law of conservation of energy**. During a physical or chemical change, the energy may be converted from one form into another but the total energy remains constant. It states that

energy can neither be created nor destroyed although it can be converted from one form into another.

This law holds good in chemical reactions also. Energy may be absorbed or evolved in chemical reaction but the total energy of the reacting system and the surroundings remains constant. This law has been stated in several other ways but the basic idea remains the same *i.e.*, conservation of energy. For example, the law can also be stated as

(i) the total energy of the universe remains constant.

(ii) The energy of the system that is isolated from its surroundings (i.e., isolated system) is constant

Justification for the First Law of Thermodynamics

The first law of thermodynamics has **no theoretical proof.** It is a law based on human experience and has not yet been violated. The following observations justify the validity of this law :

(*i*) It is not possible to construct a perpetual machine which can do work without the expenditure of energy. If the law were not true, it would have been possible to construct such a machine.

(*ii*) James Joule (1850) conducted a large number of experiments regarding the conversion of work into heat energy. He concluded that for every 4.183 joule of work done on the system, one calorie of heat is produced. He also pointed out that the same amount of work done always produces same amount of heat irrespective of how the work is done.

(*iii*) Energy is conserved in chemical reactions also. For example, the electrical energy equivalent to 286.4 kJ mol^{-1} of energy is consumed when one mole of water decomposes into gaseous hydrogen and oxygen. On the other hand, the same amount of energy in the form of heat is liberated when one mole of liquid water is produced from gases hydrogen and oxygen.

$$H_2O(l) + 286.4 \text{ kJ} \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + 286.4 \text{ kJ}$$

These examples justify that energy is always conserved though it may change its form.

Mathematical Expression for the First Law of Thermodynamics

Let us consider a general case in which a change of state is brought both by doing work and by transfer of heat.

The internal energy of a system can be changed in two ways :

(*i*) By allowing heat to flow into the system or out of the system.

(*ii*) By doing work on the system or by the system.

Let us consider a system whose internal energy is U_1. Now, if the system absorbs q amount of heat, then the internal energy of the system increases and becomes $U_1 + q$.

If work w is done on the system then its internal energy further increases and becomes U_2. Thus,

$$U_2 = U_1 + q + w$$

$$U_2 - U_1 = q + w$$

or $$\Delta U = q + w \quad \ldots(i)$$

i.e. (**Change in internal energy**) = (**Heat added to the system**) + (**Work done on the system**)

The above relationship is a **mathematical statement** of first law of thermodynamics.

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If a system does work (w) on the surroundings, its internal energy decreases. In this case, work is taken as negative ($-w$). Now, if q is the amount of heat added to the system and w is the work done by the system, then change in internal energy becomes

$$\Delta U = q + (-w) = q - w \qquad ...(ii)$$

$$i.e. \begin{pmatrix}\textbf{Change in}\\ \textbf{internal energy}\end{pmatrix} = \begin{pmatrix}\textbf{Heat added to}\\ \textbf{the system}\end{pmatrix} - \begin{pmatrix}\textbf{Work done by}\\ \textbf{the system}\end{pmatrix}$$

The above relationship between internal energy, work and heat is a mathematical **statement of first law of thermodynamics.**

Substituting the value of $w = -p_{ex}\Delta V$, in eqn. (i), we get,

$$\Delta U = q - p_{ex}\Delta V \qquad ...(iii)$$

If the process is carried out at **constant volume**,

$\Delta V = 0$ so that,

$\Delta U = q_v$

The subscript v in q_v indicates that heat is supplied at constant volume. Thus, if a reaction is carried out at constant temperature and constant volume then no work is done and the heat exchanged with the surroundings is equal to change in internal energy. Thus, the change in internal energy (ΔU) of a reaction is equal to heat evolved or absorbed during the reaction at constant temperature and constant volume.

ΔU = Heat absorbed or evolved in a reaction at constant temperature and volume

For isothermal changes in an ideal gas, for example, expansion into vacuum at constant temperture :

$$\Delta U = 0$$

because $w = 0$ ($p_{ex} \times \Delta V = 0 \times \Delta V = 0$) and $q = 0$. Joule experimentally found $q = 0$. Since U is a state function, $\Delta U = 0$ for all isothermal processes, reversible as well as irreversible.

Thus, the general expression,

$\Delta U = q + w$ may be expressed for isothermal irreversible and reversible changes as :

For **isothermal irreversible change,**

$q = -w = p_{ex}\ (V_f - V_i)$

where V_i is initial volume and V_f is final volume

For **isothermal reversible change,**

$$q = -w = nRT\ ln\ \frac{V_f}{V_i}$$

$$\text{or} = 2.303\ nRT \log \frac{V_f}{V_i}$$

$$\text{or} = 2.303\ nRT \log \frac{p_i}{p_f}$$

where p_i is initial pressure and p_f is final pressure

For **adiabatic change**, $q = 0$ so that,

$$\Delta U = w_{ad}$$

It should be noted that

- *Energy is a state function and ΔU depends only on the initial and final states whereas q and w are not state functions.* The values of q and w depend upon the way in which the change is carried out. However, whatever may be the process, ΔU is always equal to $q + w$ and, therefore, $q + w$ is also a state function.
- For an **ideal gas undergoing an isothermal change,** *the internal energy of the system does not change i.e.,* $\Delta U = 0$, then

  $0 = q + w$ or $q = -w$.

  This means that heat absorbed by the system is equal to the negative of the work done on the system or equal to work done by the system.

Sign Conventions for Heat and Work

It is very important to understand the sign conventions for q and w.

The signs of w and q are related to the internal energy change. When w or q are positive, it means that energy has been supplied to the system as work or as heat. The internal energy of the system in such a case **increases**.

On the other hand, if w or q is negative, it means that energy has left the system as work or heat. The internal energy of the system in such a case **decreases.**

Let us illustrate these conventions :

If heat is absorbed by a system, q is **positive** (since there is increase in energy of the system) but if heat is evolved by a system q is given **negative** sign (since there is loss in energy of the system). For example, if we supply 25 kJ of heat energy to the system, we write q = + 25 kJ but if same amount of heat is given out to the surroundings, we write q = – 25 kJ.

When work is done on the system, w is **positive** (energy of the system increases). But if system does work on the surroundings, w is **negative** (energy of the system decreases because work is done at the cost of energy). For example, if 15 kJ of energy is transferred to the system by doing work on the system, we write w = + 15 kJ. But if the system does 15 kJ of work on the surroundings, we write w = –15 kJ because the system has lost 15 kJ of energy.

Heat absorbed by the system = **q positive**
Heat evolved by the system = **q negative**
Work done on the system = **w positive**
Work done by the system = **w negative**

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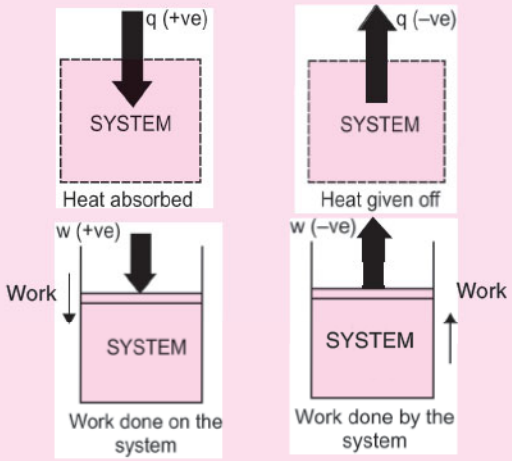
- **Thus, in general**

w and q are positive if energy (as work and heat) enters the system and w and q are negative if energy (as work and heat) leaves the system



Zeroth law of thermodynamics. This law put forward the concept of temperature on a firm basis as a property which is independent of the composition of the system. It states that *if a system A is in thermal equilibrium with a system C and if a system B is also in thermal equilibrium with the system C, then A and B are also in thermal equilibrium with each other, whatever the composition of the system.*

A ⇌ C B ⇌ C

It means that A and B are also in thermal equilibrium.

A ⇌ B

SOLVED EXAMPLES

Example 2.

Express the change in internal energy of a system when

(i) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have ?

(ii) No work is done on the system, but q amount of heat is taken out from the system and given to the surroundings. What type of wall does the system have ?

(iii) w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be ? ***N.C.E.R.T.***

Solution: (i) Since no heat is absorbed by the system,

$$q = 0$$

$$\therefore \quad \Delta U = q + w = 0 + w_{adiabatic}$$

$$\therefore \quad \Delta U = w_{adiabatic}$$

As no heat is absorbed by the system, the wall is **adiabatic.**

(*ii*) Here, $w = 0$ and $q = -q$

$$\therefore \quad \Delta U = q + w = -q + 0 = -q$$

Since heat is taken out, the system must be having **thermally conducting wall.**

(*iii*) Here, $w = -w$, $q = +q$

$$\therefore \quad \Delta U = q + w = q + (-w) = q - w$$

Since work is done by the system on absorbing heat, it must be a **closed system.**

Example 3.

Calculate the internal energy change for each of the following processes :

(i) A system absorbs 428 J of heat and does work equivalent to 286 J on its surroundings.

(ii) 62 J of work is done on the system and 128 J of heat is transferred to the surroundings.

Solution: (*i*) Heat absorbed by the system = 428 J

or $q = 428$ J

Work done by the system = 286 J

or $w = -286$ J

According to first law of thermodynamics

$$\Delta U = q + w$$

$$\Delta U = 428 - 286 = \mathbf{142\ J}$$

Thus, internal energy of the system **increases** by **142 J.**

(*ii*) Work done on the system = 62 J

or $w = 62$ J

Heat given out by the system = 128 J

or $q = -128$ J

Now $\Delta U = q + w$

$= -128 + 62 = -66$ J

Thus, internal energy of the system **decreases** by **66 J**.

Example 4.

2L of an ideal gas at a pressure of 10 atm expands isothermally into a vacuum until its total volume is 10L.

(i) How much heat is absorbed and how much work is done in the expansion ?

(ii) How much heat is absorbed if this system expands against a constant external pressure of 1 atm ?

(iii) How much heat is absorbed if the expansion is conducted reversibly at 298 K.

Solution: When the system is conducted isothermally, $\Delta U = 0$

so that $q = -w = p_{ex}\,\Delta V = p_{ex}\,(10 - 2)$

$= 0 \times 8 = 0$

$\because$ expansion occurs in vacuum, $p_{ex} = 0$

No work is done ; no heat is absorbed

(*ii*) $q = -w = p_{ex}(8) = 1 \times 8 = 8$ litre. atm

(*iii*) $q = -w = 2.303\ nRT \log \frac{V_2}{V_1}$

$= 2.303\ pV \log \frac{V_2}{V_1}$

$= 2.303 \times 10 \text{ atm} \times 2\text{L} \log \frac{10}{2}$

$= 2.303 \times 10 \text{ atm} \times 2\text{L} \times 0.699$

$= 32.2$ L atm.

$= 32.2 \times 101.3$ J = **3.26 kJ.**

Remember **1 L atm = 101.3 J**

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Example 5.

A gas absorbs 120 J of heat and expands against the external pressure of 1.10 atm from a volume of 0.5 L to 2.0 L. What is the change in internal energy ? (1 L atm = 101.3 J)

Solution: Work of expansion,

$$w = -p\,\Delta V$$
$$\Delta V = 2.0 - 0.5 = 1.5\ L,\ p = 1.10\ atm$$
$$p\Delta V = -1.10 \times 1.5$$
$$= -1.650\ L\ atm$$
$$= -1.650 \times 101.3 \quad (1\ L\ atm = 101.3\ J)$$
$$= -167.1\ J$$

Since work is done by the system, $w = -167.1$ J

Heat absorbed by the system = 120 J or $q = +120$ J

Now, $\Delta U = q + w$

$= 120\ J + (-167.1) = \mathbf{-47.1\ J}$

Example 6.

Calculate ΔU, q and w when 2.0 mol of an ideal gas at 25°C are compressed isothermally and reversibly from 1.0 bar to 10.0 bar.

Solution: For an isothermal compression,

$$\Delta U = 0$$

$$w = 2.303\ nRT \log \frac{p_2}{p_1}$$

Here $n = 2.0$ mol, $p_1 = 1.0$ bar, $p_2 = 10.0$ bar

$$\therefore \quad w = 2.303 \times (2.0\ mol)\ (8.314\ JK^{-1}\ mol^{-1}) \times (298\ K) \log \frac{10.0}{1.0}$$
$$= 2.303 \times 2.0 \times 8.314 \times 298 \times 1\ J$$
$$= \mathbf{11.412\ kJ}$$

Now $\Delta U = q + w$

For isothermal expansion of ideal gas, $\Delta U = 0$

$$0 = q + w \quad \text{or} \quad q = -w$$
$$\therefore \quad q = \mathbf{-11.412\ kJ}$$

Example 7.

Three moles of hydrogen gas are compressed isothermally and reversibly from 60 L to 20 L and 8.50 kJ of work is done on it. Assuming ideal behaviour, calculate the temperature of the gas.

Solution: Since the gas behaves ideally, reversible work of compression is given by

$$w = 2.303\ nRT \log \frac{V_2}{V_1}$$

Here $n = 3$ mol, $V_1 = 60$ L, $V_2 = 20$ L, $w = 8.5 \times 10^3$ J

$$8.50 \times 10^3\ J = 2.303 \times (3)\ (8.314)\ T \log \frac{60}{20}$$
$$= 2.303 \times 3 \times (8.314)\ T \times 0.4771$$
$$8.50 \times 10^3\ J = 27.405\ T\ JK^{-1}$$
$$\therefore \quad T = \frac{8.50 \times 10^3\ J}{27.405\ JK^{-1}} = \mathbf{310\ K}$$

Example 8.

Calculate w and ΔU for the conversion of 1 mol of water at 100° C to steam at 1 atm pressure. Heat of vaporisation of water at 100°C is 40.670 kJ mol^{-1}. Assume ideal gas behaviour.

Solution: $p = 1$ atm

V_1 = Vol. of 1 mole of liquid water at 1 atm

$= 18\ mL = 18 \times 10^{-3}\ L$

V_2 = Vol. of 1 mole of steam at 100°C at 1 atm pressure

$$V_2 = \frac{nRT}{p}$$
$$= \frac{1\ mol \times 0.0821\ L\ atm\ K^{-1}\ mol^{-1} \times 373\ K}{1\ atm}$$
$$= 30.6\ L$$
$$p_{ext}\Delta V = p_{ext}\,(V_2 - V_1)$$
$$= 1\ atm\ (30.6 - 18 \times 10^{-3})\ L$$
$$= 30.582\ L\ atm$$
$$= 30.582 \times 101.3\ J \quad (1\ L\ atm = 101.3\ J)$$
$$= 3098\ J = 3.098\ kJ$$

Since conversion of water to steam is accompanied by increase in volume, work is done by the system on surroundings. Hence w is negative, by convention,

$$w = -3.098\ kJ$$

Now

$$\Delta U = q + w$$
$$= 40.670 - 3.098 = \mathbf{37.572\ kJ}$$

Example 9.

A 6-litre cylinder contained 280 g of N_2 gas at 27° C. Due to sudden leakage through the hole, all the gas escaped into atmosphere and the cylinder became empty. If the atmospheric pressure is 1.0 atmosphere, calculate the work done by the gas.

Solution:

$$V_{initial} = 6\ L,\ T = 273 + 27 = 300\ K$$
$$n = \frac{280}{28} = 10\ mol,\ p = 1\ atm$$
$$V_{final} = \frac{nRT}{p}$$
$$= \frac{10\ mol \times (0.0821\ L\ atm\ mol^{-1}\ K^{-1}) \times (300K)}{(1.0\ atm)}$$
$$= 246.3\ L$$
$$\Delta V = V_{final} - V_{initial} = 246.3 - 6.0 = 240.3\ L$$
$$w_{exp} = -p\Delta V$$
$$= -1\ atm \times 240.3\ L$$
$$= -240.3\ L\ atm$$
$$= -240.3 \times 101.3\ J \quad (\because 1\ L\ atm = 101.3\ J)$$
$$= \mathbf{-24.342\ kJ}$$

Practice Problems

3. A system gives out 30 J of heat and does 75 J of work. What is the internal energy change ?

4. During a process, a system absorbs 710 J of heat and does work. The change in internal energy for the process is 460 J. What is the work done by the system ?

5. Four moles of an ideal gas at 2.5 atm and 27° C are compressed isothermally to half of its volume by an external pressure of 3 atm. Calculate w, q and ΔU.

6. A gas expands isothermally from 10 dm^3 to 20 dm^3 at 27° C and work obtained is 4.620 kJ. Calculate the number of moles of the gas.

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Answers to Practice Problems

3. –105 J **4.** –250 J
5. 5981 J, –5981 J, 0 **6.** 2.67 mol

Hints & Solutions on page 78

ENTHALPY AND ENTHALPY CHANGE: A USEFUL NEW STATE FUNCTION

The change in internal energy gives the heat change accompanying a chemical reaction at constant volume i.e., $\Delta U = q_v$. However, in laboratory, most of the chemical reactions are carried out at constant pressure rather than at constant volume. For example, all systems open to atmosphere are obviously at constant atmospheric pressure. When a chemical reaction takes place in an open atmosphere, there may be change in volume but the pressure remains constant *i.e.,* atmospheric pressure. To study the heat changes for reactions at constant pressure and at constant temperature, a new term called **enthalpy** has been introduced. We have learnt that internal energy change may be expressed as :

$$\Delta U = q_p - p\Delta V \text{ at constant temperature} \quad ...(i)$$

where q_p is the heat absorbed by the system and $-p\Delta V$ represents expansion work done by the system.

Let us represent initial state by subscript 1 and final state by 2 so that

$$\Delta U = U_2 - U_1 = q_p - p\,(V_2 - V_1)$$

On rearranging

$$q_p = (U_2 + pV_2) - (U_1 + pV_1) \quad ...(ii)$$

We can define another thermodynamic function, enthalpy , H (Greek word *enthalpien* to warm) or heat content as,

$$H = U + pV$$

so that eqn. (*ii*) becomes

$$q_p = H_2 - H_1 = \Delta H$$

Although q is path dependent function, q_p is independent of path. Thus, H is a state function (H is function of U, p and V, which are all state functions). Thus, ΔH is independent of path. Thus, **enthalpy** of a system may be defined as

the sum of the internal energy and the product of its pressure and volume.

It is denoted by the symbol H and is given by

$$H = U + pV$$

where U is the internal energy, p is the pressure and V is the volume of the system. Enthalpy is also called **heat content.** Since H depends upon three state functions U, p and V, it is also a state function.

Every substance has a definite value of enthalpy in a particular state. Like internal energy, the absolute value of enthalpy cannot be measured. However, the change in enthalpy accompanying a process can be determined. Thus for a process represented as :

$$A \longrightarrow B$$

The change in enthalpy may be expressed as :

$$\Delta H = H_B - H_A$$

where H_A is the enthalpy of state A and H_B is the enthalpy of state B and ΔH is the enthalpy change. For a chemical reaction, ΔH can be given as difference between the enthalpies of the products and the reactants *i.e.,*

$$\Delta H = H_{products} - H_{reactants}$$
$$= H_p - H_r$$

where H_p is the enthalpy of the products, H_r is the enthalpy of the reactants and ΔH is the enthalpy change.

If a reaction is carried out at constant temperature and constant pressure, the heat exchanged by the system with the surroundings (*i.e.,* heat change) is equal to change in enthalpy. Thus,

the enthalpy change of a reaction is equal to the heat absorbed or evolved during a reaction at constant temperature and pressure.

ΔH= Heat evolved or absorbed in a reaction at constant temperature and constant pressure

It may be noted that the amount of heat exchanged with the surroundings for a reaction at constant pressure (ΔH) is different from that exchanged at constant volume (ΔU) and temperature. This can be easily understood. At constant pressure, the volume of the reacting system changes. If the volume increases, the system expands against the atmospheric pressure and energy is required for this expansion. Therefore, a part of energy will be used for the expansion. As a result, the amount of heat exchanged at constant pressure (ΔH) would be less than the amount of heat exchanged at constant volume (ΔU).

Alternatively, if the system contracts at constant pressure, work is done on the system and the system absorbs some energy from the surroundings. Therefore, the amount of heat exchanged at constant pressure is greater than that exchanged at constant volume.

Significance of ΔU and ΔH and First Law of Thermodynamics

Significance of ΔU and ΔH follows from the first law of thermodynamics. According to first law of thermodynamics :

$$\Delta U = q + w$$

Let the change in volume during the process at constant p is ΔV, then work is referred to as *pressure-volume* work and it is given as $p\Delta V$. When a gas expands, work is done by the system on the surroundings and pressure-volume work, $w = -p\Delta V$, so that

$$\Delta U = q - p\Delta V$$

or

$$q = \Delta U + p\Delta V \quad ...(i)$$

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If the process is carried out at constant volume, *i.e.,* $\Delta V = 0$, then the product $p\Delta V$ is also zero. Thus,

$$q_v = \Delta U \qquad ...(ii)$$

The change in internal energy is equal to heat absorbed or evolved at constant volume and constant temperature.

Now, enthalpy is defined as

$$H = U + pV$$

Change in enthalpy, ΔH may be expressed as

$$\Delta H = \Delta U + \Delta(pV) \qquad ...(iii)$$

$$\Delta H = \Delta U + p\Delta V + V\Delta p$$

If the process is carried out at constant pressure, *i.e.,* $\Delta p = 0$, then

$$\Delta H = \Delta U + p\Delta V \qquad ...(iv)$$

Now, $\Delta U = q + w$

If work done during the change is only expansion work,

$$w = -p\Delta V \text{ so that}$$

$$\Delta U = q - p\Delta V$$

Substituting in Eq. (*i*), the value of ΔU, we get

$$\Delta H = q - p\Delta V + p\Delta V = q$$

$$\therefore \quad \Delta H = q_p \text{ (at constant pressure)} \qquad ...(v)$$

where q_p indicates that heat change has taken place at constant pressure. Thus,

the enthalpy change is a measure of heat change (evolved or absorbed) taking place during a process at constant pressure.

Thus, we can sum up :

If q is the amount of heat absorbed by the system.

q (at constant volume) = ΔU

q (at constant pressure) = ΔH

Relationship between ΔH and ΔU

Consider a reaction

$$A \longrightarrow B$$

at constant pressure, p. Let H_A be the enthalpy of the reactants and H_B be the enthalpy of products so that change in enthalpy, ΔH may be

$$\Delta H = H_B - H_A$$

But $H = U + pV$

Let U_A and V_A be the internal energy and volume of the reactants and U_B and V_B be the corresponding values for the products. Therefore,

$$H_A = U_A + pV_A \text{ and } H_B = U_B + pV_B$$

$$\therefore \quad \Delta H = (U_B + pV_B) - (U_A + pV_A)$$

or $$\Delta H = (U_B - U_A) + p(V_B - V_A)$$

or $$\Delta H = \Delta U + p\Delta V \qquad ...(vi)$$

where ΔU is the change in internal energy and ΔV is the change in volume of the system.

The difference between ΔH and ΔU is not usually significant for solids and liquids. However, when the systems involve gases, the difference becomes significant. Consider a chemical reaction taking place at a constant temperature (T) and pressure (p). Let V_A is the total volume of the gaseous reactants and V_B is the total volume of the gaseous products, n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products. According to ideal gas equation,

$$pV = nRT$$

For reactants,

$$pV_A = n_A RT \quad \text{(at constant T and } p) \qquad ...(vii)$$

For products,

$$pV_B = n_B RT \quad \text{(at constant T and P)} \qquad ...(viii)$$

Subtracting Eq. (*vii*) from Eq. (*viii*), we get

$$p(V_B - V_A) = n_B RT - n_A RT$$

or $$= (n_B - n_A) RT$$

or $$p\Delta V = \Delta n_g RT \qquad ...(ix)$$

where Δn_g is the change in the number of gaseous moles of products and gaseous moles of reactants.

Thus, Eq. (*vi*) becomes

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\begin{bmatrix}\text{Energy change}\\ \text{at constant } p\end{bmatrix} = \begin{bmatrix}\text{Energy change}\\ \text{at constant V}\end{bmatrix} + \begin{bmatrix}\text{Change in the}\\ \text{number of}\\ \text{gaseous moles}\end{bmatrix} \times RT$$

This relation is very useful for converting ΔH into ΔU or ΔU into ΔH.

Thus,

$$\Delta H = \Delta U + p\Delta V$$

$$\Delta H = \Delta U + \Delta n_g RT$$

It is **important to note** that ΔH will be equal to ΔU under the following conditions :

(*i*) *Reactions which do not involve any gaseous components.* For example, reaction between aqueous solution of hydrochloric acid and sodium hydroxide.

$$HCl\,(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

(*ii*) *Reactions carried out in closed vessels of fixed volume i.e.,* $\Delta V = 0$.

(*iii*) *Reactions which involve gaseous reactants and products but there is no change in the number of moles of the gaseous components.*

For example,

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

In all such reactions, the volume change is zero *i.e.* $\Delta n_g = 0$

$$\therefore \quad \Delta H = \Delta U + \Delta n_g RT = \Delta U + 0 \times RT = \Delta U$$

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However, in gaseous reactions having Δn_g not equal to zero, ΔH and ΔU will be different. For example :

(*i*) *Reactions in which there is an increase in the number of moles of the gaseous components.* In such cases, Δn_g is positive and consequently, the enthalpy change (ΔH) is greater than the internal energy change (ΔU), *i.e.*, $\Delta H > \Delta U$. Some examples of such reactions are given below :

$$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g) ;$$

$$[\Delta n_g = (1 - \frac{1}{2}) = + \frac{1}{2}]$$

$$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g) ;$$

$$[\Delta n_g = (2 - 1) = + 1]$$

(*ii*) *Reactions in which there is a decrease in the number of moles of the gaseous components.* In such cases, Δn_g is negative and consequently, the enthalpy change (ΔH) is less than the internal energy change (ΔU), *i.e.*, $\Delta H < \Delta U$. Some examples of such reactions are given below :

$$CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g) ;$$

$$[\Delta n_g = (1 - 1\frac{1}{2}) = - \frac{1}{2}]$$

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) ;$$

$$[\Delta n_g = (2 - 4) = - 2]$$

Thus, for gaseous reactions, the difference between ΔH and ΔU depends upon the value of Δn_g. For example,

$\Delta n_g = 0$; $\Delta H = \Delta U$

$\Delta n_g =$ –ve ; $\Delta H < \Delta U$

$\Delta n_g =$ +ve ; $\Delta H > \Delta U$

SOLVED EXAMPLES

Example 10.

The heat of combustion of gaseous methane (CH_4) at constant volume is measured in a bomb calorimeter at 298 K and is found to be –885.4 kJ mol^{-1}. Find the value of enthalpy change.

Solution: Combustion of methane gives $CO_2(g)$ and $H_2O(l)$ as :

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$\Delta U = -885.4$ kJ mol^{-1} $= -885400$ J mol^{-1}

$\Delta n_g = 1 - (1 + 2) = -2$ mol.

T = 298 K, R = 8.314 J mol^{-1} K^{-1}

Now, $\Delta H = \Delta U + \Delta n_g RT$

$= -885400 + (-2 \text{ mol}) \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})$

$= -885400 - 4955$

$= -890355 =$ **–890.355 kJ**

Example 11.

The enthalpy change (ΔH) for the reaction :

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

is –92.38 kJ at 298 K. What is ΔU at 298 K ?

N.C.E.R.T.

Solution: ΔH and ΔU are related as

$\Delta H = \Delta U + \Delta n_g RT$

For the reaction,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

$\Delta n_g = 2 - (1 + 3) = -2$ mol, T = 298 K

$\Delta H = -92.38$ kJ $= -92380$ J, R = 8.314 J K^{-1} mol^{-1}

$-92380 = \Delta U + (-2 \text{ mol}) \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})$

$-92380 = \Delta U - 4955$

$\Delta U = -92380 + 4955 = -87425$ J = **–87.425 kJ**

Example 12.

Enthalpy of combustion of carbon to CO_2 (g) is –393.5kJ mol^{-1}. Calculate the heat released upon the formation of 35.2g of CO_2 from carbon and dioxygen gas.

N.C.E.R.T.

Solution: $C(s) + O_2(g) \rightarrow CO_2(g)$

$\Delta H = -393.5$ kJ mol^{-1}

Heat released for the formation of 44g (1mol) of $CO_2 = 393.5$ kJ

Heat released for the formation of 35.2 g of CO_2

$= \frac{393.5 \times 35.2}{44} =$ **314.8 kJ**

Example 13.

If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1 bar and 100°C is 41 kJ mol^{-1}. Calculate the internal energy change, when

(a) 1 mol of water is vaporised at 1 bar pressure and 100°C.

(b) 1 mol of water is converted into ice.

N.C.E.R.T.

Solution: (*a*) $H_2O(l) \longrightarrow H_2O(g)$

$\Delta H = \Delta U + \Delta n_g RT$

or $\Delta U = \Delta H - \Delta n_g RT$

$\Delta H = 41.0$ kJ mol^{-1}, $\Delta n_g = 1 - 0 = 1$, T = 273 + 100 = 373 K

R = 8.314 J mol^{-1} K^{-1} = 8.314 × 10^{-3} kJ mol^{-1} K^{-1}

$\therefore \quad \Delta U = 41.0 - 1 \times 8.314 \times 10^{-3} \times 373$

$= 41.0 - 3.10 =$ **37.90 kJ mol^{-1}**

(*b*) $H_2O(l) \longrightarrow H_2O(s)$

There is negligible change in volume so that

$p\Delta V = \Delta n_g RT = 0$

$\therefore \quad \Delta U = \Delta H =$ **41.0 kJ mol^{-1}**

Example 14.

The heat liberated on complete combustion of 7.8 g of benzene at constant volume at 25°C has been found to be 326.39 kJ. Calculate the heat of combustion of benzene at constant pressure.

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Solution: Heat of combustion of benzene at constant volume,

$$\Delta U = -\frac{326.39}{7.8} \times 78 = -3263.9 \text{ kJ mol}^{-1}$$

(molecular mass of benzene, $C_6H_8 = 78$)

The reaction is:

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(l)$$

$$\Delta n_g = 6 - \frac{15}{2} = \frac{-3}{2}$$

$$\Delta H = \Delta U + \Delta n_g\, RT$$

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$

$T = 273 + 25 = 298 \text{ K}$

$$\Delta H = -3263.9 + \left(-\frac{3}{2}\right) \times 8.314 \times 10^{-3} \times 298$$

$$= -3263.9 - 3.72 = \mathbf{-3267.62\ kJ}\ \text{mol}^{-1}$$

Practice Problems

7. The enthalpy changes for the following reactions at 298 K and 1 atm are given below :

(*i*) $CH_3COOH(l) + 2O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$; $\Delta H = -874$ kJ

(*ii*) $CH_3CH_2OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$; $\Delta H = -1363$ kJ

Calculate the internal energy changes for these reactions :

8. The enthalpy of combustion of benzoic acid (C_6H_5COOH) at 298 K and 1 atm pressure is -2546.0 kJ mol^{-1}. What is ΔU for the reaction ?

9. Gaseous N_2O decomposes at 298 K and forms N_2 (*g*) and O_2 (*g*). The ΔH for the reaction at 1 atm pressure and 298 K is -163.15 kJ. What is the value of ΔU for the decomposition of 200 g of N_2O under the same conditions?

Answers to Practice Problems

7. (*i*) – 874 kJ (*ii*) –1360.5 kJ

8. -2544.8 kJ mol^{-1}

9. –376.39 kJ

Hints & Solutions on page 78

EXOTHERMIC AND ENDOTHERMIC REACTIONS

The chemical reactions are often accompanied by evolution or absorption of energy. Depending upon the evolution or absorption of energy they are classified into two types : *exothermic* and *endothermic reactions.*

1. Exothermic reactions

The chemical reactions which proceed with the evolution of heat energy are called **exothermic reactions.** The heat energy produced during the reactions is indicated by writing + *q* or more precisely by giving the actual numerical value on the products side. In general, exothermic reactions may be represented as :

$$A + B \longrightarrow C + D + q \text{ (heat energy)}$$

We have already learnt that the heat evolved at constant pressure and constant temperature is equal to the enthalpy change (ΔH). In the exothermic reactions, the enthalpy of the products will be less than the enthalpy of the reactants so that the enthalpy change which is the total enthalpy of products minus the total enthalpy of reactants is negative as shown below :

$$\Delta H = H_p - H_r$$

Now, $H_p < H_r$

$\therefore$ $\Delta H = -\text{ve}$

For example, one mole of carbon reacts with one mole of oxygen to form one mole of carbon dioxide and 393.5 kJ of heat is evolved at constant temperature and constant pressure. The reaction may be expressed as

$$C(s) + O_2(g) \longrightarrow CO_2(g) + 393.5 \text{ kJ}$$

or $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -393.5$ kJ

Some other examples of exothermic reactions are :

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta H = -285.8$ kJ

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta H = -92.3$ kJ

$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$; $\Delta H = -694.6$ kJ

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$; $\Delta H = -890.3$ kJ

2. Endothermic reactions

The chemical reactions which proceed with the absorption of heat energy are called **endothermic reactions.** Since the heat is added to the reactants in these reactions, the heat absorbed is indicated by either putting + *q* or by writing the actual numerical value of heat on the reactants side.

$$A + B + q \text{ (heat)} \longrightarrow C + D$$

Alternatively, it may be written as :

$$A + B \longrightarrow C + D - q \text{ (heat)}$$

The heat absorbed at constant temperature and constant pressure measures enthalpy change. Because of the absorption of heat, the enthalpy of the products will be more than the enthalpy of the reactants. Consequently, ΔH will be positive (+ve) for the endothermic reactions.

$$\Delta H = H_p - H_r$$

$H_p > H_r$ $\quad\therefore\ \Delta H = +\text{ve}$

For example, one mole of nitrogen reacts with one mole of oxygen to form two moles of nitric oxide and 180.5 kJ of heat is absorbed at constant temperature and the reaction may be expressed as :

$$N_2(g) + O_2(g) + 180.5 \text{ kJ} \longrightarrow 2NO(g)$$

or $N_2(g) + O_2(g) \longrightarrow 2NO(g)$; $\Delta H = +180.5$ kJ

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Some other examples of endothermic reactions are:

$$C(s) + 2S(s) \longrightarrow CS_2(l); \quad \Delta H = +92.0 \text{ kJ}$$

$$H_2(g) + I_2(g) \longrightarrow 2HI(g); \quad \Delta H = +53.9 \text{ kJ}$$

$$2HgO(s) \longrightarrow 2Hg(l) + O_2(g); \quad \Delta H = +180.4 \text{ kJ}$$

$$SnO_2(s) + 2C(s) \longrightarrow Sn(s) + 2CO(g); \quad \Delta H = +360.0 \text{ kJ}$$

The enthalpy changes for exothermic and endothermic reactions are shown in Fig. 9 (*a*) and (*b*).

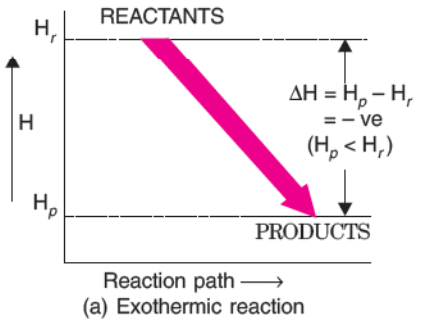

Fig. 9. (*a*) Enthalpy change during an exothermic reaction.

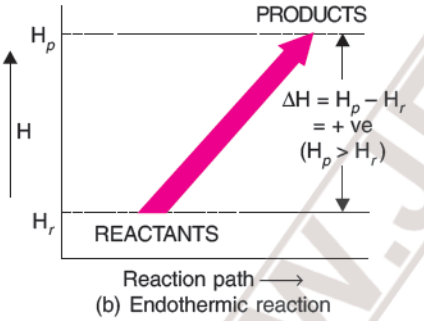

Fig. 9. (*b*) Enthalpy change during endothermic reaction.

Similarly, if we consider heat change at constant volume and temperature, ΔU is –ve for *exothermic reactions* and ΔU is +ve for endothermic reactions.

Thus, it may be **concluded** that

For **exothermic reactions,** ΔH or ΔU = **–ve**

For **endothermic reactions,** ΔH or ΔU = **+ve**

HEAT CAPACITY

The heat changes from or into the system appear as changes in temperature. If a system absorbs heat, its temperature rises and if a system gives heat its temperature falls. The increase or decrease of temperature is proportional to the heat transferred *i.e.*,

$$q = \text{coeff} \times \Delta T$$

where q is the heat (gained or lost) transferred, ΔT is the change in temperature and magnitude of the coefficient depends on the size, composition and nature of the system. We may also write

$$q = C\,\Delta T$$

The coefficient C, is called the heat capacity. When C is large, a given amount of heat results in only a small rise in temperature. But when C is small, a given amount of heat results in a large rise in temperature. So, if we know, heat capacity of a substance, we can measure the heat supplied by knowing the rise in temperature. Water has a large heat capacity and therefore, a lot of energy is needed to raise its temperature. Thus, **heat capacity** is defined as

the amount of heat required to raise the temperature of the system by one degree.

It can be simply calculated by dividing the heat absorbed by the increase in temperature. If q is the heat absorbed by the system and ΔT is the rise in temperature then the heat capacity*, C is

$$\text{Heat capacity} = \frac{\text{Heat absorbed}}{\text{Rise in temperature}}$$

or

$$C = \frac{q}{\Delta T} \qquad ...(i)$$

If q is in Joules (J) and ΔT is in Kelvin (K) or Celsius (°C), the units of heat capacity are Joules/Kelvin (J K^{-1}) or Joules/Celsius (J/°C). For example, if we supply 98 kJ of heat to a sample of ethanol, its temperature rises by 2K, then

$$\text{Heat capacity} = \frac{q}{\Delta T} = \frac{98 \text{ kJ}}{2K} = 49 \text{ J } K^{-1}$$

Heat capacity depends upon whether the sample is maintained at constant volume (like a gas in a sealed vessel) or the sample is maintained at constant pressure (like water in an open vessel). So, heat capacity is of two types :

(i) **Heat capacity determined at a constant volume abbreviated as C_v**

(ii) **Heat capacity determined at a constant pressure, abbreviated as C_p.**

Heat capacity at constant pressure is more common than heat capacity at constant volume.

For solids and liquids, there is not much difference between the values of C_p and C_v. However, for gases these quantities differ.

If we change the temperature of the sample from initial temperature T_i to a final temperature T_f, then the heat required will be,

*Since heat capacity varies with temperature, it may be expressed for infinitesimally small changes in temperature. If dq is the very small quantity of heat absorbed and dT is the infinitesimally small rise in temperature, then heat capacity, C may be defined as

$$C = \frac{dq}{dT}$$

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$$q = C_v . \Delta T \text{ or } q = C_p \Delta T$$
$$\text{where } \Delta T = T_f - T_i$$

Suppose a piece of metal requires 6.80 J of heat to raise its temperature by one degree celsius at constant volume. Then, heat capacity at constant volume,

$$C_v = 6.80 \text{ J/°C}$$

Now, if we want to raise the temperature of the piece of metal from 25°C to 100°C, then quantity of heat required '*q*' will be,

$$q = C_v \Delta T$$
$$= (6.80 \text{ J/°C}) \times (100 - 25)\text{°C}$$
$$= 510.0 \text{ J}.$$

More heat is required to raise the temperature of a large sample of substance by 1°C than needed for a small sample of the same substance. In other words, *the larger the sample, the greater its heat capacity.* It is therefore, common to use *specific heat capacity* (or simply specific heat) or *molar heat capacity.* These are defined as :

the heat required to raise the temperature of 1 gram of a substance by one degree (1 K or 1°C) is called ***specific heat capacity or simply specific heat.***

$$\text{Specific heat} = \frac{\text{Heat absorbed}}{\text{Rise in temperature} \times \text{Mass of sample in gram}}$$

The units of specific heat are J K^{-1} g^{-1} (SI units) or J $°C^{-1}$ g^{-1}. For example, the specific heat of liquid water is 4.18 J K^{-1} g^{-1}.

The amount of heat required to raise the temperature of 1 mole of a substance by one degree (1 K or 1° C) **is called *molar heat capacity.***

i.e. $C_m = \frac{C}{n}$

where *n* is the number of moles of the substance and C_m is the molar heat capacity.

$$\text{or Molar heat capacity} = \frac{\text{Heat absorbed}}{\text{Rise in temperature} \times \text{Molar mass}}$$

The units of molar heat capacity are J K^{-1} mol^{-1} (SI units) or J$°C^{-1}$ mol^{-1}.

The molar heat capacity of water is 75.4 JK^{-1} mol^{-1}.

Since the molar mass of water is 18 g/mol, the molar heat capacity of water is 18 times its specific heat capacity. Thus, the relationships between heat capacity, specific heat capacity and molar heat capacity are :

$$\text{Heat capacity} = \text{Specific heat capacity} \times \text{Mass}$$

$$\text{or Specific heat capacity} = \frac{\text{Heat capacity}}{\text{Mass}}$$

$$\text{Molar heat capacity} = \frac{\text{Heat capacity}}{\text{Molar mass}}$$

or Molar heat capacity = Specific heat capacity × Molar mass

If we know the mass of the substance, its specific heat capacity and the rise in temperature during the experiment, heat supplied to it may be calculated as :

Heat supplied = Mass (g) × Specific heat capacity (J K^{-1} g^{-1}) × Rise in temperature (K)

i.e. $q = m \times C_s \times \Delta T$

REMEMBER

The difference between heat capacity, specific heat capacity and molar heat capacity can be easily understood. Let a piece of copper metal weighing 5 g requires 3.85 J of heat to raise the temperature from 298 K to 300 K. Then,

- Heat capacity of copper = $\frac{3.85 \text{ J}}{2 \text{ K}} = 1.925 \text{ J K}^{-1}$
- Specific heat capacity of copper = $\frac{3.85 \text{ J}}{5\text{g} \times 2\text{K}}$ $= 0.385 \text{ Jg}^{-1} \text{ K}^{-1}$
- Molar heat capacity of copper $= \frac{3.85 \text{ J}}{5\text{g} \times 2\text{K}} \times 63.5\text{g mol}^{-1} = 24.45 \text{ J mol}^{-1} \text{ K}^{-1}$.

The specific heat capacities of some common materials are listed in Table 1.

Table 1. Specific Heat Capacities of Some Common Materials.

Substance	Specific heat capacity
Air	0.72
Benzene	1.05
Copper	0.385
Aluminium	0.902
Gold	0.128
Iron	0.460
Brass	0.37
Stainless steel	0.51
Ethanol	2.46
Ammonia (liquid)	4.70
Ethylene glycol	2.42
Carbon tetrachloride	0.861
Glass (pyrex)	0.78
Polyethylene	2.3
Water, solid	2.03
liquid	4.18
vapour	2.01

It may be noted that **heat capacity is extensive property but specific heat capacity and molar heat capacity are intensive properties.**

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From thermodynamics, it may be shown that heat capacity at constant volume gives the rate of change of internal energy with temperature, *i.e.*

$$C_v = \left(\frac{\Delta U}{\Delta T}\right)_v \quad \text{or} \quad = \left(\frac{dU}{dT}\right)_v$$

Heat capacity at constant pressure gives the rate of change of enthalpy with temperature, *i.e.*

$$C_p = \left(\frac{\Delta H}{\Delta T}\right)_p \quad \text{or} \quad = \left(\frac{dH}{dT}\right)_p$$

It may be noted that sometimes the symbols $\overline{C}_v$ and $\overline{C}_p$ are used to denote heat capacities per mole. Therefore, if n is the number of moles of the substance in the system, then :

$$C_v = n \times \overline{C}_v \qquad \text{and} \qquad C_p = n \times \overline{C}_p$$

Relationship between C_p and C_v

The two heat capacities are not equal, but **C_p is greater than C_v.** Let us find out relationship between these two heat capacities.

At constant volume, heat absorbed

$$q_v = C_v \Delta T = \Delta U \qquad ...(ii)$$

at constant pressure, heat absorbed

$$q_p = C_p \Delta T = \Delta H \qquad ...(iii)$$

The difference between C_p and C_v can be derived for an ideal gas as :

For 1 mole of an ideal gas,

$$\Delta H = \Delta U + p\Delta V$$

or $$\Delta H = \Delta U + \Delta(RT)$$

$$= \Delta U + R\Delta T$$

$\therefore \Delta H = \Delta U + R\Delta T$ for 1 mole of an ideal gas. Substituting the values of ΔH and ΔU,

$$C_p\Delta T = C_v\Delta T + R\Delta T$$

or $$C_p = C_v + R$$

$\therefore$ $$C_p - C_v = R \qquad ...(iv)$$

for 1 mole of an ideal gas.

Similarly, for n moles of an ideal gas.

$$C_p - C_v = nR \qquad ...(v)$$

The difference is due to the work involved in changing its volume. At constant volume, no external work is done. Therefore, all the heat supplied to the system is used in increasing its internal energy. However at constant pressure, there will be increase in the volume of the system and some external work will be done. In other words, at constant pressure, a part of heat absorbed is utilised in increasing its internal energy and a part of heat is utilised in doing external work. Therefore, some extra heat must be supplied to the system to enable it to perform this external work.

It may be noted that the ratio C_p/C_v (represented by γ) gives information about the atomicity of a gas. The C_p/C_v values for different types of gases are :

Nature of gas	Monoatomic	Diatomic	Triatomic non-linear
$\gamma\ (C_p/C_v)$	1.66	1.40	1.33

Advanced Level Note

Relationship between p, V and T for adiabatic expansion of an ideal gas

pV^γ = constant or $p_1V_1^{\ \gamma} = p_2V_2^{\ \gamma}$

$TV^{\gamma-1}$ = constant or $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$T^\gamma p^{1-\gamma}$ = constant or $T_1^{\ \gamma}p_1^{\ 1-\gamma} = T_2^{\ \gamma}p_2^{\ 1-\gamma}$

or $T\,p^{(1-\gamma)/\gamma}$ = constant or $T_1p_1^{(1-\gamma)/\gamma} = T_2p_2^{(1-\gamma)/\gamma}$

where $\gamma = C_p/C_v$

SOLVED EXAMPLES

Example 15.

A swimming pool contains 1×10^5 L of water. How much energy in joules is required to raise the temperature of water from 20°C to 25°C ? The specific heat capacity of water is 4.184 J/°C g.

Solution:

Heat supplied = Mass × Specific heat capacity × Rise in temperature

$= m \times C_s \times \Delta T$

$m = 1 \times 10^5\ L = 1 \times 10^5 \times 10^3$

$= 1 \times 10^8$ g (density = 1 g cm^{-3})

C_s = 4.184 J/°C g

$\Delta T = 25 - 20 = 5°$

$\therefore$ Heat supplied $= 1 \times 10^8 \times 4.184 \times 5$

$= 2.092 \times 10^9$ J

or $= \mathbf{2.092 \times 10^6\ kJ}$

Example 16.

(a) Calculate the heat that must be supplied to raise the temperature of 2 kg of water from 25°C to its boiling point at atmospheric pressure. The average specific heat of water in the range 25–100°C is 4.184 J K^{-1} g^{-1}.

(b) How long will a 2 kW heater take to supply this energy ?

Solution: (*a*) Heat required for heating $= m \times C_s \times \Delta T$

m = 2000 g, $\Delta T = 100 - 25 = 75°$, $C_s = 4.184$ J K^{-1} g^{-1}.

$\therefore$ Heat required $= 2000 \times 4.184 \times 75$

$= 6.28 \times 10^5$ J

or $= 6.28 \times 10^2$ kJ

(*b*) Heat supplied by 2 kW heater = 2000 J s^{-1}

Time required to supply 6.28×10^2 kJ of heat

$$= \frac{6.28 \times 10^2 \times 10^3\ \text{J}}{2000\ \text{J s}^{-1}} = 314\ \text{s}$$

or $= \mathbf{5\ min\ 13.8\ s}$

Example 17.

(a) Calculate the energy needed to raise the temperature of 10.0 g of iron from 25°C to 250°C if specific heat capacity of iron is 0.45 J °C^{-1} g^{-1}.

(b) What mass of copper (specific heat capacity = 0.385 J °C^{-1} g^{-1}) can be heated through the same temperature difference when supplied with the same amount of energy as above.

Solution: (*a*) Mass of iron = 10.0° g

Rise in temperature, $\Delta T = 250° - 25° = 225°C$

Specific heat capacity of iron = 0.45 J °C^{-1} g^{-1}

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Energy needed = $m \times C_s \times \Delta T$

= 10.0 (g) × 0.45 J (°C)$^{-1}$ g^{-1} × 225°C

= **1012.5 J = 1.012 kJ**

(b) Specific heat capacity of copper

= 0.385 J °C^{-1} g^{-1}

ΔT = 225°C

Energy = 1012.5

Energy = $m \times C_s \times \Delta T$

1012.5 = $m \times 0.385 \times 225$

$\therefore \quad m = \frac{1012.5}{0.385 \times 225} =$ **11.6 g**

❑ Example 18.

A chemist while studying the properties of gaseous $C_2Cl_2F_2$, a chorofurorocarbon refeigerant cooled a 1.25 g sample at constant atmospheric pressure of 1.0 atm from 320 to 293 K. During cooling, the sample volume decreased from 274 to 248 mL. Calculate ΔH and ΔU for the chloroflurocarbon for this process. For $C_2Cl_2F_2$, C_p = 80.7 J/mol K.

N.C.E.R.T.

Solution: Fall in temperature = 320 – 293 = 27K

Molar mass of $C_2Cl_2F_2$ = 2 × 12 + 2 × 35.5 + 2 × 19

= 133

C_p = 80.7 J mol^{-1} K^{-1}

or $= \frac{80.7}{133} = 0.6068$ J g^{-1} K^{-1}

Heat evolved from 1.25 g of sample on being cooled

$q_p = m \times C_p \times \Delta T$

= 1.25 g × 0.6068 J K^{-1} g^{-1} × 27 K

= 20.48 J

$\therefore \quad \Delta H$ = –20.48 J

Now $\Delta H = \Delta U + p\Delta V$

$p\Delta V = 1 \text{ atm} \times \frac{(248-274)}{1000}$ L

= – 0.026 L atm

= – 0.026 × 101. 325 = – 2.63 J

– 20.48 = ΔU – 2.63

ΔU = – 20.48 + 2.63

= **– 17.84 J.**

❑ Example 19.

Calulate the number of kJ necessary to raise the temperature of 60.0 g of aluminium from 35° to 55° C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.

N.C.E.R.T.

Solution: Mass of aluminium = 60g.

Rise in temperture ΔT = 55 – 35 = 20° C

Molar heat capacity of Al = 24 J mol^{-1} K^{-1}

Specific heat capacity of Al $= \frac{24}{27} = 0.889$ Jg^{-1}K^{-1}

Energy required = m × C × ΔT

= 60 × 0.889 × 20

= **1066.8 J or 1.07 kJ**

MEASUREMENT OF INTERNAL ENERGY (ΔU) AND ENTHALPY (ΔH) OF REACTION

When a system absorbs or releases energy in the form of heat, its temperature changes. This change in temperature can be measured. From this, the heat evolved during the process can be calculated. Measurement of energy changes are carried out under different conditions :

(i) at constant volume, q_v, which gives change in internal energy, ΔU.

(ii) at constant pressure, q_p, which gives change in enthalpy, ΔH.

The heat absorbed at constant volume for chemical reactions is measured with a bomb calorimeter. The measurements of energy changes at constant pressure are very common because many physical and chemical processes take place in open *i.e.*, at constant pressure. There are different methods which are in use for the determination of the enthalpy of reaction. But the commonly employed method for the experimental determination of enthalpy of a reaction is **calorimetry**. The apparatus used for this purpose is known as ***calorimeter.*** Although the basis for calorimetry is almost the same, yet different types of calorimeters are used for different types of chemical reactions.

Simple calorimeter or water calorimeter.

This type of calorimeter is employed usually for determining the heat changes accompanying the chemical reactions taking place in solutions. The apparatus consists of a water bath having insulated walls. There is another vessel in which a reaction is carried and is called a reaction chamber. The reaction chamber is immersed in the water bath. A water bath is also provided with the stirring arrangement and an accurate thermometer (Fig. 10).

An ordinary vacuum flask which is provided with a thermometer and a stirrer, can also serve as a simple calorimeter.

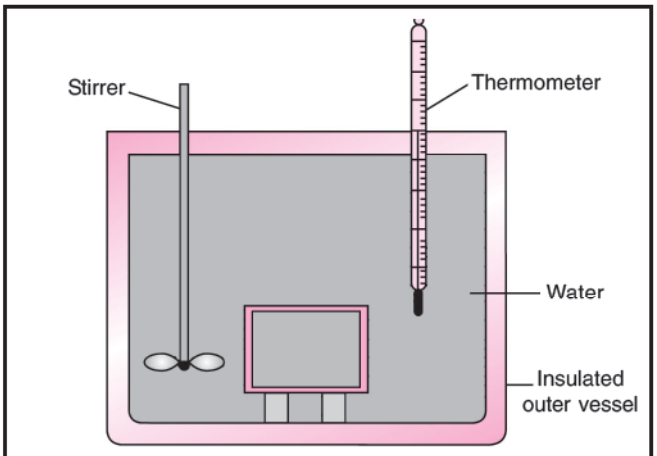

Fig. 10. A simple calorimeter for measuring heat changes at constant pressure.

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A simple cup calorimeter commonly used in the laboratory is shown in Fig. 11. The outer polystyrene cup acts as an extra layer of insulation to ensure that no heat enters or leaves the inner cup.

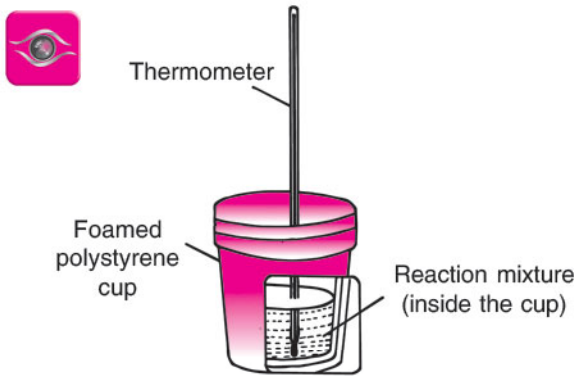

Fig. 11. A simple calorimeter commonly used in laboratory.

Since these calorimeters are open to the atmosphere, so these measure heat changes at constant presure (q_p or ΔH).

Procedure. First of all the heat capacity of the calorimeter is found. For this purpose, a known weight W_1 g of water is taken in the water bath at room temperature t_1 and W_2 g of a hot water at the temperature, t_2 is added to it. Stirring is continuously done till the temperature of mixture becomes constant (t_3).

Then the heat capacity of the calorimeter is

$$= \frac{W_2(t_2 - t_3)}{(t_3 - t_1)} \times W_1.$$

Now, once again a known weight W of water is taken in the bath at a temperature 't'. The reaction chamber carrying a known weight of the reactants is immersed in the bath and the reaction is allowed to take place. If the reaction is exothermic, the temperature of the water in the bath increases. On the other hand, if the reaction is endothermic, the temperature of the water in the bath decreases. Stirring is continuously done in order to keep the temperature uniform. The change in the temperature of water is noted. Let it be Δt.

The heat produced or absorbed during the reaction is calculated as follows :

$$\text{Heat changes during the reaction} = \begin{bmatrix}\text{Heat capacity of} \\ \text{the calorimeter}\end{bmatrix} \times \Delta t \times \begin{bmatrix}\text{Specific heat} \\ \text{of water}\end{bmatrix}$$

This simple calorimeter has been modified in various forms.

Bomb calorimeter.

This type of calorimeter is mainly used for determining the **heat of combustion** of fuels such as, coal, kerosene oil, petrol, etc. This gives the heat absorbed at constant volume. It consists of a strong metallic chamber which is commonly known as a **bomb**. The bomb is made of heavy steel and is capable of withstanding a high pressure which develops inside due to the gases produced as a result of combustion. The steel vessel is also lined inside with gold or platinum alloy or some other non-oxidisable substance to check the oxidation of steel during the chemical reactions. It is fitted with a pressure tight screw cap cover and is also provided with platinum cup where the combustion is carried out (Fig. 12). The two firing leads are connected to each other through a platinum wire dipping in the platinum cup C.

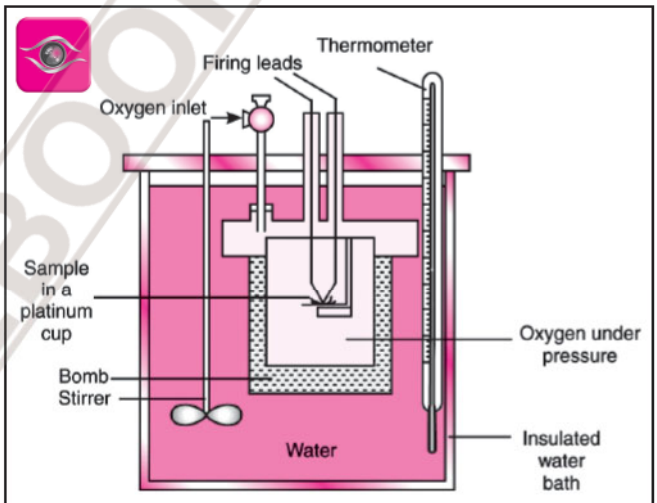

Fig. 12. Bomb calorimeter for the determination of change in internal energy.

A small known amount of the substance under investigation is taken in the platinum cup. The bomb is filled with excess of oxygen under pressure of 20–25 atmospheres and is sealed. It is then lowered in an insulated water bath which contains a known quantity of water. The water bath is also provided with a mechanical stirrer and a **Beckmann thermometer** which can read correctly upto 0.01°.

The initial temperature of water is noted and reaction, *i.e.* combustion is started by passing an electric current through the platinum wire. The heat energy evolved during the chemical reaction raises the temperature of water which is carefully recorded from the thermometer. By knowing the rise in temperature (Δt) and the heat capacity of the calorimeter, the amount of heat evolved in the reaction can be calculated.

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Heat of combustion is calculated as follows :

$$\text{Heat produced during combustion} = \begin{bmatrix}\text{Heat capacity}\\ \text{of calorimeter}\end{bmatrix} \times \Delta t \times \begin{bmatrix}\text{Specific heat}\\ \text{of water}\end{bmatrix}$$

Now, if heat capacity of calorimeter system including water is Z and Δt is the rise in temperature for burning m gm of a substance having molecular weight M. Then the heat of combustion of a substance is given by $Z \times \Delta t \times \frac{M}{m}$ joules.

It may be noted that in this case volume remains constant. Therefore, value of heat of combustion calculated by this method is a measure of ΔU. However, ΔH value can be calculated further by applying the relation :

$$\Delta H = \Delta U + \Delta n_g RT$$

SOLVED EXAMPLES

Example 20.

0.562 g of graphite kept in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure was burnt according to the reaction :

$$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g)$$

During the reaction the temperature rises from 298 K to 298.80 K. If the heat capacity of the magnitude calorimeter and its contents is 20.7 kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm ?

Solution: Quantity of heat absorbed by the calorimeter

$$q = C_v \times \Delta T$$

$$\Delta T = 298.89 - 298 = 0.089\ K,\ C_V = 20.7\ kJ/K$$

$$\therefore \quad q = 20.7 \times 0.89 = 18.433\ kJ$$

Quantity of heat produced = 20.7 kJ

Heat produced by burning 0.562 g of graphite

$$= -18.423\ kJ$$

Heat produced by burning 1 mol (12 g) of graphite

$$= \frac{-18.423 \times 12}{0.562}$$

$$= -393.4\ kJ$$

$\therefore$ Enthalpy of combustion of graphite, $\Delta H = -393.4\ kJ\ mol^{-1}$

Example 21.

The reaction of cyanamide $[NH_2CN(s)]$ with dioxygen was carried out in a bomb calorimeter and ΔU was found be $-742.7\ kJ\ mol^{-1}$ at 298K. Calculate enthalpy change for the reaction at 298 K :

$$NH_2CN(s) + \frac{3}{2} O_2\ (g) \rightarrow N_2\ (g) + CO_2\ (g) + H_2O(l)$$

Solution: $\Delta H = \Delta U + \Delta n_g RT$

$$\Delta U = -742.7\ kJ\ mol^{-1},\ \Delta n_g = 1 + 1 - \frac{3}{2} = \frac{1}{2}$$

$$\therefore \Delta H = -742.7\ kJ\ mol^{-1} + \frac{1}{2} \times 8.314 \times 10^{-3}\ kJ\ mol^{-1}\ K^{-1} \times 298K$$

$$= -742.7 + 1.2$$

$$= -741.5\ kJ\ mol^{-1}$$

Practice Problems

10. A 1.250 g sample of octane (C_8H_{18}) is burned in excess of oxygen in a bomb calorimeter. The temperature of calorimeter rises from 294.05 K to 300.78 K. If heat capacity of calorimeter and its contents is 8.93 kJ/K, calculate the heat transferred to calorimeter. **N.C.E.R.T.**

11. 20 g of ammonium nitrate (NH_4NO_3) is dissolved in 125 g of water in a coeffee-cup calorimeter, the temperature of which falls from 296.5 K to 286.4 K. Find the value of q for the calorimeter (Treat heat capacity of water as the heat capacity of the calorimeter and its contents). **N.C.E.R.T.**

12. 1g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298K and 1 atmospheric pressure according to the equation :

$$C\ (\text{graphite}) + O_2\ (g) \rightarrow CO_2\ (g)$$

During the reaction, temperature rises from 298 K to 299 K . If the heat capacity of the bomb calorimeter is 20.7 kJ K^{-1}, what is the enthalpy change for the above reaction at 298 K and 1 atm ? **N.C.E.R.T.**

Answers to Practice Problems

10. 60.1 kJ

11. 5.285 kJ

12. $-2.48 \times 10^2\ kJ\ mol^{-1}$.

Hints & Solutions on page 78

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add on

Conceptual Questions 1

CONCEPTUAL QA

Q.1. Under what conditions is the heat of reaction equal to enthalpy change ?

Ans. The heat of reaction is equal to enthalpy change at constant pressure *i,e.*,

$$q_p = \Delta H$$

Q.2. Identify the kind of energy change usually associated with each of the following ;

***(a)* automobile engine** ***(b)* fluorescent lamp**
***(c)* radio** ***(d)* friction**
***(e)* phtoelectric cell**

Ans. *(a)* Chemical energy into mechanical energy
(b) Electrical energy to light
(c) Electrical energy to sound energy
(d) Mechanical energy to heat energy
(e) Light to electric energy.

Q.3. Show that the product of pressure and volume i.e., *p*V has the dimensions of energy.

Ans. $p \times V$

$$= \frac{\text{Force}}{\text{Area}} \times \text{Volume} = \frac{\text{Force} \times (\text{Length})^3}{(\text{Length})^2} = \text{Force} \times \text{Length} = \text{Work} = \text{Energy}.$$

Q.4. Neither *q* nor *w* is a state function but *q* + w is a state function. Explain why ?

Ans. $q + w$ is equal to ΔU which is a state function.

Q.5. What will happen to internal energy if work is done by the system ?

Ans. The internal energy of the system will decrease if work is done by the system.

Q.6. Is there any enthalpy change in a cyclic process ?

Ans. No, there is no enthalpy change in a cyclic process because the system returns to the initial state.

Q.7. Why do we feel cold on touching ice ?

Ans. Ice absorbs heat from our hands.

Q.8. How many times is molar heat capacity than specific heat capacity of water ?

Ans. 18 times .

Q.9. Which of the following are state functions ?
(*i*) *q* (*ii*) heat capacity (*iii*) specific heat capacity (*iv*) $\Delta_r H°$ (*v*) *w*.

Ans. *(iii)* and *(iv)*

Q.10. Explain why heat capacity is not a state function ?

Ans. Heat capacity , $C = q / \Delta T$. Since 'q' is not a state function, therefore, C is also not a state function.

Q.11. What is the enthalpy change when 1.0 g of water is frozen at 0°C? $\Delta_{fus} H = 6.02$ kJ mol^{-1}.

Ans. $\Delta H = -\frac{6.02 \times 10^3 \text{ J mol}^{-1}}{18} = -334.4 \text{ J g}^{-1}$.

Q.12. Heat capacity is an extensive property but specific heat is intensive property. Comment on the statement.

Ans. Heat capacity depends upon the mass of the substance and therefore, it is an extensive property. But specific heat is the heat capacity per unit mass and therefore, becomes independent of amount of substance. Hence specific heat is intensive property.

Q.13. Which out of force and pressure is intensive property ?

Ans. Pressure is intensive property because it is force exerted per unit area.

Q.14. The C_p and C_v of a gas are 20.834 and 12.520 JK^{-1} mol^{-1} respectively. What is the atomicity of the gas.

Ans. $\frac{C_p}{C_v} = \frac{20.834}{12.520} = 1.66$. Therefore, the gas is **monoatomic** gas.

Q.15. Why heat changes reported are usually enthalpy changes and not internal energy changes?

Ans. This is because most of the processes are carried out in open vessels i.e., at constant pressure.

Q.16. What is the relation for work done (*i*) reversibly and (*ii*) irreversibly for the isothermal expansion of an ideal gas from volume V_1 to V_2 at temperature T ?

Ans. *(i)* $w_{rev} = -2.303\, n\text{RT} \log \frac{V_2}{V_1}$ *(ii)* $w_{irrev} = -p\,(V_2 - V_1)$

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ENTHALPY CHANGES OF CHEMICAL REACTIONS : REACTION ENTHALPIES

The amount of heat evolved or absorbed in a reaction is known as heat of reaction. Since the amount of heat evolved or absorbed at constant temperature and pressure is called enthalpy, the heat changes for various reactions may also be called enthalpy changes. The heat change during a chemical reaction depends upon the amount of substance (number of moles) that has reacted. Thus, **enthalpy of reaction** may be defined as

the enthalpy change (amount of heat evolved or absorbed) in a reaction when the number of moles of reactants react completely to give the products as given by the balanced chemical equation.

For example, the enthalpy change for the reaction of one mole of methane with two moles of oxygen to form one mole of CO_2 and two moles of water is –890.3 kJ *i.e.*, 890.3 kJ of heat is evolved during this reaction. Thus,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g); \quad \Delta_r H = -890.3 \text{ kJ}$$

Factors on which Enthalpy Change (ΔH) of a Reaction Depends

The enthalpy change of reaction ($\Delta_r H$) depends upon the following factors :

1. Physical state of the reactants and the products. The ΔH of a reaction depends upon the physical states of reactants and products. For example, when hydrogen and oxygen gases combine to give liquid water, the enthalpy of reaction is different than when they combine to form gaseous water etc.

$$H_2(g) + O_2(g) \longrightarrow H_2O(l); \Delta_r H = -285.8 \text{ kJ}$$
$$H_2(g) + O_2(g) \longrightarrow H_2O(g); \Delta_r H = -241.8 \text{ kJ}$$

2. Quantities of reactants. The enthalpy change (or amount of heat evolved or absorbed) depends upon the amount of reactants. For example, the heat of combustion of 2 moles of carbon is double than heat of combustion of 1 mole of carbon.

3. Allotropic modification. The enthalpy change for different allotropic forms of the same substance are different. For example,

$$C \text{ (diamond)} + O_2(g) \longrightarrow CO_2(g); \Delta_r H = -395.4 \text{ kJ}$$
$$C \text{ (graphite)} + O_2(g) \longrightarrow CO_2(g); \Delta_r H = -393.5 \text{ kJ}$$

4. Temperature. The enthalpy of reaction depends upon the temperature of reactants and products.

5. Condition of constant pressure or volume. The enthalpy of reaction depends upon the conditions of constant pressure or volume. We have already studied,

$$q_v = \Delta U \text{ and } q_p = \Delta H$$

and $$\Delta H = \Delta U + p\Delta V$$

ΔH may be equal, greater than or less than ΔU.

Standard Enthalpy of Reaction

It may be noted that the enthalpy of a reaction depends upon the conditions of the reaction, *i.e.* temperature and pressure. Therefore, it is convenient to fix up a standard or a reference state. According to thermodynamic convention, **a substance is said to be in standard state when it is present in its most stable state under a pressure of 1 bar at a specified temperature.** For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 298 K and 1 bar pressure, the standard state of solid iron at 500 K is pure iron at 500K and 1bar presure. The enthalpy change that occurs when a process is carried out at one bar pressure is called **standard enthalpy.** Thus, **standard enthalpy change** of a reaction **is the enthalpy change for a reaction when all the participating substances (elements and compounds) are in their standard states.** It is represented as ΔH° or $\Delta H^\ominus$ where the **superscript '°' or '⊖' indicates the standard state.**

⇒Earlier, the standard pressure was taken as 1 atm. But now IUPAC has recommended 1 bar as the standard pressure for defining standard thermodynamic quantities.

⇒It may be noted that temperature is not the part of the definition of standard state. It is not restricted to 25°C, rather it can be expressed at any temperature. 25°C or 298.15 K is simply the most common temperature used in thermochemical data.

Enthalpy Changes of Reactions

In a reaction, reactants are converted into products as

$$\text{Reactants} \longrightarrow \text{Products}$$

The enthalpy change of a reaction can be measured as the difference between the sum of enthalpies of products and sum of enthalpies of reactants as

$$\Delta_r H = \begin{pmatrix}\text{Sum of enthalpies of}\\ \text{products}\end{pmatrix} - \begin{pmatrix}\text{Sum of enthalpies of}\\ \text{of reactants}\end{pmatrix}$$

This may also be expressed as :

$$\Delta_r H = \sum a_i H_{\text{products}} - \sum b_i H_{\text{reactants}}$$

Here symbol, $\sum$ (sigma) is used for summation and a_i and b_i are the stoichiometric coefficients of the products and the reactants respectively in the balanced equation. For the reaction :

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta_r H = \sum_i a_i H \text{ (products)} - \sum_i b_i H \text{ (reactants)}$$

$$= \{H_m[CO_2(g)] + 2H_m[H_2O(l)]\} - \{H_m[CH_4(g)] + 2H_m[O_2(g)]\}$$

where H_m is the molar enthalpy.

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If the reaction occurs at standard state, then to calculate enthalpy of reaction at standard state, $\Delta_r H^\circ$, the enthalpy of reactants and products are taken at standard states i.e.,

$$\Delta_r H^\circ = \sum_i a_i H^\circ_m \text{ (products)} - \sum_i b_i H^\circ_m \text{ (reactants)}$$

Enthalpy change is a very useful quantity. Its knowledge is required when one needs to plan the heating or cooling required to maintain an industrial chemical reaction at constant temperature. It is also required to calculate temperature dependence of equilibrium constant.

SOLVED EXAMPLES

Example 22.

Red phosphorus reacts with liquid bromine as :

$2P\,(s) + 3Br_2(l) \longrightarrow 2PBr_3\,(g)\ \ \Delta_r H^o = -243\ kJ$

Calculate the enthalpy change when 10.32 g of phosphorus reacts with an excess of bromine.

N.C.E.R.T.

Solution: $2P(s) + 3Br_2(l) \longrightarrow 2PBr_3\,(g)$

$\Delta_r H^o = -243\ \text{kJ mol}^{-1}$

Molar mass of phosphorus $= 31\ \text{g mol}^{-1}$

Mass of P $= 10.32\ g$

Moles of P $= \dfrac{10.32}{31} = 0.333$ mol

Enthalpy change for 2 mol of P $= -243$ kJ

Enthalpy change for 0.333 mol of P

$$= \frac{-243}{2} \times 0.333$$

$$= \mathbf{-40.46\ kJ}$$

THERMOCHEMICAL EQUATIONS

A *chemical balanced equation which gives the heat change (evolved or absorbed, ΔH) during the reaction* is called the thermochemical equation.

A thermochemical equation can be written as follows :

(a) by writing the heat evolved or absorbed as a term in the equation,

$$C(s) + O_2(g) \longrightarrow CO_2(g) + 393.5\ \text{kJ}$$

$$C_2H_5OH\,(l) + 3O_2\,(g) \longrightarrow 2\,CO_2\,(g) + 3H_2O\,(l) + 1367\ \text{kJ mol}^{-1}$$

(b) by using ΔH notation, *i.e.*, writing ΔH = – ve for exothermic and ΔH = +ve for endothermic reactions, as

$$C(s) + O_2\,(g) \longrightarrow CO_2(g);\ \Delta H = -393.5\ \text{kJ mol}^{-1}$$

$$C_2H_5OH\,(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

$$\Delta H = -1367\ \text{kJ mol}^{-1}$$

Conventions for Writing the Thermochemical Equations

The following are the important **conventions** for writing the thermochemical equations :

1. For exothermic reaction, ΔH is –ve and for endothermic reaction, ΔH is + ve.
2. Unless otherwise mentioned in a given reaction, the ΔH values correspond to the standard states of the substances. ***The standard state is taken as pure form of the substance at 1 atmospheric pressure.*** The modern definition of standard state replaces 1 atm by 1 bar where 1 bar = 10^5 Pa. This has been used in the present text.
3. According to IUPAC (1981 recommendations), the different types of thermodynamic property changes such as enthalpy are expressed in such a way that the symbol denoting the process is written as a subscript before the symbol of property. For example,

   enthalpy of reaction is written as $\Delta_r H$

   enthalpy of vaporisation is written as $\Delta_{vap} H$

   enthalpy of formation is written as $\Delta_f H$

   enthalpy of combustion is written as $\Delta_c H$

   The standard state is represented by adding the superscript '⊖' or 'o' to the symbol ΔH. *i.e.*, $\Delta_r H^\ominus$ or $\Delta_r H^\circ$ etc.
4. While writing the thermochemical equation for a reaction, the physical states of the reactants and the products must be mentioned. The physical states are represented by the symbols *s*, *l*, *g* and *aq* for solid, liquid, gaseous and aqueous states respectively. The allotropic state may also be mentioned.

   It is essential because the physical states of the reactants and the products cause appreciable difference in the value of ΔH. For example, when one mole of liquid water is formed from gaseous hydrogen and gaseous oxygen, the heat evolved is equal to 285.8 kJ.

   $$H_2(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l);\quad \Delta_r H = -285.8\ \text{kJ}$$

   On the other hand, when one mole of water in the gaseous state is formed from the gaseous oxygen and hydrogen, the heat evolved is equal to 241.8 kJ

   $$H_2(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O(g);\quad \Delta_r H = -241.8\ \text{kJ}$$
5. The coefficients of the substances in a thermochemical equation represent the number of moles of each substance involved in the reaction. The ΔH values correspond to these coefficients.

   When the coefficients in the chemical equation are multiplied or divided by a factor, ΔH value must also be multiplied or divided by the same factor. For example, in the equation,

   $$H_2(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(g);\quad \Delta_r H = -241.8\ \text{kJ}$$

   If coefficients are multiplied by 2, we write the equation,

   $$2H_2(g) + O_2\,(g) \longrightarrow 2H_2\,O(g);\quad \Delta_r H = -483.6\ \text{kJ}$$

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6. When the chemical equation is reversed, the sign of ΔH value is also changed but the magnitude remains the same. For example,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g); \quad \Delta_r H = -91.8 \text{ kJ}$$
$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g); \Delta_r H = 91.8 \text{ kJ}$$

Thus, a reaction which is exothermic in one direction will be endothermic in reverse direction.

7. The value of $\Delta_r H$ usually show very small change with increase in temperature (provided there are no phase changes when the temperature is increased).

The enthalpy changes taking place during the chemical reactions are generally expressed in different ways depending upon the nature of the reaction. The various types of enthalpies of reactions are discussed ahead :

ENTHALPY OF FORMATION

The enthalpy change (or heat change) when 1 mole of a substance is formed from its elements in their most stable forms is called **enthalpy of formation.**

It is denoted by $\Delta_f H$ where the subscript '*f*' indicates that one mole of the compound has been formed from its elements in their most stable states of aggregation. The formation of carbon dioxide and methane (CH_4) may be expressed as :

$$C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = \Delta_f H = -393.5 \text{ kJ}$$
$$C(s) + 2H_2(g) \longrightarrow CH_4(g); \quad \Delta H = \Delta_f H = -74.8 \text{ kJ}$$

Similarly, enthalpy of formation of mercuric chloride and methyl alcohol may be expressed as :

$$Hg(l) + Cl_2(g) \longrightarrow HgCl_2(s)$$
$$\Delta_f H = -224.30 \text{ kJ}$$

$$C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l)$$
$$\Delta_f H = -239.0 \text{ kJ}$$

KEY NOTE

- The equation for enthalpy of formation should always be written for one mole (because of definition) of the substance to be formed. If for balancing, we require the coefficient 2, 3.... etc., in the equation, then ΔH values should also be multiplied by the same number. For example, enthalpy of formation of NH_3 may be written as :

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g); \quad \Delta_f H = -46.1 \text{ kJ}$$

However, if we want to get rid of fractions as $\frac{1}{2}$ and $\frac{3}{2}$ we may write

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

But, this corresponds to formation of 2 moles of NH_3 and ΔH will be – 92.2 kJ

- Enthalpy of formation corresponds to the formation of the compounds from its elements. For example, the enthalpy change of the reaction given below :

$CaO(s) + CO_2(g) \longrightarrow CaCO_3 : \Delta_r H^\circ = -178.3 \text{ kJ mol}^{-1}$

does not correspond to enthalpy of formation of calcium carbonate. This is because it has formed from other compounds and not from its constituent elements. The reaction representing the standard enthalpy of formation of $CaCO_3(s)$ would be

$$Ca(s) + C(s) + \frac{3}{2}O_2(g) \longrightarrow CaCO_3(s);$$
$$\Delta_r H^\circ = \Delta_f H^\circ$$

Standard enthalpy of formation

The enthalpy of formation $\Delta_f H$ depends upon the conditions of temperature, pressure and physical state (gas, liquid or solid) of the reactants and the products. If all the species of the chemical reaction are in their standard state (*i.e.*, stable forms at one bar pressure) the enthalpy of formation is called standard enthalpy of formation, expressed as $\Delta_f H^\circ$. Thus,

the enthalpy change accompanying the formation of one mole of a compound from its elements, all the substances being in their standard states is called **standard molar enthalpy of formation.**

For example :

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$$
$$\Delta_f H^\circ = -285.8 \text{ kJ mol}^{-1}$$

$$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)$$
$$\Delta_f H^\circ = -277.7 \text{ kJ mol}^{-1}$$

It is important to note that a standard molar enthalpy of formation is a special case of $\Delta_r H^\circ$, when 1 mol of a compound is formed from its constituent elements . However, enthaphy changes for all reactions are not enthalpy of formation. For example, consider the exothermic reaction :

$$CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$$
$$\Delta_r H^\circ = -178.3 \text{ kJ mol}^{-1}$$

The $\Delta_r H^\circ$ is not equal to enthalpy of formation of calcium carbonate because calcium carbonate has been formed from other compounds and not from its constitutent elements.

Similarly, for the reaction :

$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$ $\Delta_r H^\circ = -72.8 \text{ kJ mol}^{-1}$

the enthalpy change for the reaction is not standard enthalpy of formation, $\Delta_f H^\circ$ for HBr. Here two moles instead of one mole of the product is formed from the elements so that

$$\Delta_r H^\circ = 2\Delta_f H^\circ$$

Therefore, by dividing all coefficients in the balanced chemical equation by 2, the enthalpy of

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formation of HBr(g) may be written as :

$$\frac{1}{2}H_2(g) + \frac{1}{2}Br_2 \longrightarrow HBr(g);\ \Delta_f H^\circ = -36.4\ kJ\ mol^{-1}$$

The standard enthalpy of formation of various compounds are given in Table 2.

KEY NOTE

By convention, the standard enthalpy of formation $\Delta_f H^\circ$ of an element in its standard state is arbitrarily assumed to be zero.

The standard state of an elementary substance ***means the most stable state of aggregation of that substance at 1 atmospheric pressure. It refers to the normal physical state in which the element exists.*** For example, the standard states of oxygen, nitrogen and hydrogen are $O_2(g)$, $N_2(g)$ and $H_2(g)$ because these exist in gaseous states. On the otherhand, the standard states of bromine and iodine are $Br_2(l)$ and $I_2(s)$ because bromine exists in liquid state whereas iodine exists in solid state. In case of elements showing allotropy, standard state refers to the moststable allotropic form. For example, standard states for carbon and sulphur are C (graphite) and S_8 (rhombic) respectively.

Calculation of Standard Enthalpy of Reaction from Standard Enthalpy of Formation

The knowledge of standard enthalpies of formation of various substances can be used to calculate the enthalpies of reactions under standard conditions. In general, the standard enthalpy of any reaction ($\Delta_r H^\circ$) is equal to the difference between the $\Delta_f H^\circ$ of all the products and the reactants *i.e.*,

$\Delta_r H^\circ$ for a reaction

$$= \left[\begin{array}{c}\textbf{Sum of the standard enthalpies}\\ \textbf{of formation of products}\end{array}\right] - \left[\begin{array}{c}\text{Sum of the standard enthalpies}\\ \text{of formation of reactants}\end{array}\right]$$

$$i.e., \Delta_r H^\circ = \sum_i a_i \Delta_f H^\circ(\text{products}) - \sum_i b_i \Delta_f H^\circ\ (\text{reactants})$$

Where Σ is known as summation and means *sum of,* and a_i and b_i are the stoichiometric coefficients of the products and reactants in the balanced equation.

Enthalpy changes of a Reaction

Consider the reaction,

$$aA + bB \longrightarrow cC + dD$$

$$\Delta_r H^\circ = \Sigma \Delta_f H^\circ\ (\text{products}) - \Sigma \Delta_f H^\circ\ (\text{reactants})$$

$$= [c\Delta_f H^\circ(C) + d\Delta_f H^\circ(D)] - [a\Delta_f H^\circ(A) + b\Delta_f H^\circ(B)]$$

For example, consider the reaction of decomposition of calcium carbonate

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

$$\Delta_r H^\circ = \Delta_f H^\circ[CaO(g)] + \Delta_f H^\circ[CO_2(g)] - \Delta_f H^\circ[(CaCO_3(s)]$$

$$= (-635.1\ kJ\ mol^{-1}) + (-393.5\ kJmol^{-1}) - (-1206.9\ kJ\ mol^{-1})$$

$$= 178.3\ kJ\ mol^{-1}$$

Thus, the decomposition of $CaCO_3(s)$ is endothermic process and it is carried out by heating.

The enthalpy of formation of all elements in their standard states are arbitrarily assumed to be zero. On this basis, it is evident that *the enthalpy of formation of a compound is the enthalpy of the compound as :*

$$\text{Elements} \longrightarrow \text{Compound}$$

Enthalpy of formation = H (compound) – H (elements)
= H (compound)

Table 2. Standard molar enthalpy of formation of various compounds.

Substance	$\Delta_f H^\circ$(kJ mol^{-1})
$Al_2O_3(s)$	–1675.7
$AlCl_3(s)$	– 704.2
$BaCO_3(s)$	– 1216.3
$Br_2(l)$	0.0
$Br_2(g)$	+ 30.9
C (graphite)	0.0
C (diamond)	+ 1.89
$CaO(s)$	– 635.09
$CH_4(g)$	– 74.81
$C_2H_4(g)$	+ 52.26
$C_6H_6(l)$	+ 49.03
$C_2H_6(g)$	– 84.68
$CH_3OH(l)$	– 239.0
$C_2H_5OH(l)$	–277.69
$CH_3COOH(l)$	–484.2
$CO(g)$	– 110.52
$CO_2(g)$	– 393.51
$Cl_2(g)$	0.0
$C_3H_8(g)$	– 103.85
n–$C_4H_{10}(g)$	–126.15
HgS(s) (red)	–58.2
$CaCO_3(s)$	–1206.92
$C_6H_5OH(s)$	+ 94.12
$CCl_4(l)$	– 135.44
$CS_2(l)$	+ 89.70
FeS(s)	– 95.1
$H_2(g)$	0.0
$H_2O(l)$	– 285.83
$H_2O(g)$	– 241.82
HF (g)	– 271.1
$HCl(g)$	– 92.30
$HBr(g)$	– 36.40
HI (g)	+ 26.48
$NO(g)$	+ 90.25
$NO_2(g)$	+ 33.28
$HNO_3(l)$	– 174.10
$H_2SO_4(l)$	– 811.3
$He(g)$	0.0
$H_2S(g)$	– 20.60
$HgCl_2(s)$	– 224.30

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Substance	$\Delta_f H^\circ$(kJ mol^{-1})
$I_2(s)$	0.0
$I_2(g)$	+ 62.44
KCl (s)	– 436.74
KBr(s)	– 393.8
$NH_3(g)$	– 46.11
NaCl (s)	– 411.15
$C_2H_5OH(l)$	– 360.06
NaI(s)	– 287.78
$NH_4Cl(s)$	– 314.43
$O_2(g)$	0.0
$O_3(g)$	+ 163.2
$PH_3(g)$	+ 5.4
$PCl_3(l)$	– 287.0
$PCl_3(g)$	– 319.7
$PCl_5(s)$	– 443.5
KF(s)	– 576.27
Si(s)	0.0
SiO_2 (s) (quartz)	– 910.93
$SnCl_2$ (s)	– 325.1
$SnCl_4(l)$	–511.3
$SO_2(g)$	–296.83
SO_3 (g)	– 395.72
$SiH_4(g)$	+ 34.0
$SiCl_4(g)$	–657.0
$Fe_2O_3(s)$	–824.2
C (g)	+716.68
H(g)	+ 217.97
Cl(g)	+ 121.68

SOLVED EXAMPLES

Example 23.

The enthalpy change for the reaction,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

is –92.2 kJ. Calculate the enthalpy of formation of ammonia.

Solution: The enthalpy of formation of ammonia is the enthalpy change for the formation of 1 mole of ammonia from its elements, *i.e.*,

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g); \qquad \Delta_f H^\circ = ?$$

The enthalpy change for the reaction

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

is $\Delta_r H$ = –92.2 kJ. This equation corresponds to formation of two moles of ammonia. Thus,

$$\Delta_f H^\circ = -\frac{92.2}{2} = \mathbf{-46.1\ kJ\ mol^{-1}}$$

Example 24.

Calculate the enthalpy change in the reaction :

$$4NH_3(g) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(l)$$

at 298 K given that the enthalpy of formation at 298 K for NH_3 (g) and H_2O (l) are –46.0 and –286.0 kJ mol^{-1} respectively.

Solution: $\Delta_r H^\circ$ for the reaction,

$$4NH_3(g) + 3O_2(g) \longrightarrow 6H_2O(l) + 2N_2(g)$$

$$\Delta_r H^\circ = \Delta_f H^\circ \text{ (products)} - \Delta_f H^\circ \text{ (reactants)}$$
$$= \{6\Delta_f H^\circ[H_2O(l)] + 2\Delta_f H^\circ[N_2(g)]\} - \{4\Delta_f H^\circ[NH_3(g)] + 3\Delta_f H^\circ[O_2(g)]\}$$

$\Delta_f H^\circ[H_2O(l)] = -286.0$ kJ mol^{-1}

$\Delta_f H^\circ[NH_3(g)] = -46.0$ kJ mol^{-1}

$\Delta_f H^\circ[O_2(g)] = 0$ and $\Delta H_f^\circ[N_2(g)] = 0$ (by convention)

$\therefore \quad \Delta_r H^\circ = \{6(-286) + 2(0)\} - \{4(-46.0) + 3(0)\}$
$= -1716 + 184 = \mathbf{-1532\ kJ}$

Example 25.

Calculate the enthalpy change for the reaction

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

The enthalpy of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(l)$ are –74.8 kJ mol^{-1}, –393.5 kJ mol^{-1} and –285.8 kJ mol^{-1} respectively.

Solution: $\Delta_r H^\circ$ for the reaction,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

is $\Delta_r H^\circ = \Delta_f H^\circ$ (products) $- \Delta_f H^\circ$ (reactants)
$= \{\Delta_f H^\circ[CO_2(g)] + 2\Delta_f H^\circ[H_2O(l)]\} - \{\Delta_f H^\circ[CH_4(g)] + 2\Delta_f H^\circ[O_2(g)]\}$

$\Delta_f H^\circ[CO_2(g)] = -393.5$ kJ mol^{-1},

$\Delta_f H^\circ[H_2O(l)] = -285.8$ kJ mol^{-1}

$\Delta_f H^\circ[CH_4(g)] = -74.8$ kJ mol^{-1}, $\Delta_f H^\circ[O_2(g)] = 0$ (by convention)

$\therefore \quad \Delta_r H^\circ = \{-393.5 + 2(-285.8)\} - \{-74.8 + (2 \times 0)\}$
$= -965.1 + 74.8 = \mathbf{-890.3\ kJ\ mol^{-1}}$

Example 26.

The combustion of one mole of benzene takes place at 298 K and 1 bar pressure. After combustion, CO_2 (g) and H_2O (l) are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, $\Delta_f H^\circ$ of benzene. Given that standard enthalpy of formation of CO_2 (g) and H_2O (l) are –393.5 and –285.83 kJ mol^{-1} respectively. ***N.C.E.R.T.***

Solution: Combustion of 1 mol of benzene takes place as :

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$$

$\Delta_c H^\circ = -3267.0$ kJ mol^{-1}

$\Delta_r H^\circ = \Sigma\Delta_f H^\circ$ (products) $- \Sigma\Delta_f H^\circ$ (reactants)
$= 6[\Delta_f H^\circ\{CO_2(g)\}] + 3[\Delta_f H^\circ\{H_2O(l)\}] - [\Delta_f H^\circ\{C_6H_6(l)\}] - \frac{15}{2}[\Delta_f H^\circ\{O_2(g)\}]$

$\Delta_f H^\circ\{CO_2(g)\} = -393.5$ kJ mol^{-1}, $\Delta_f H^\circ\{H_2O(l)\}$
$= -285.83$ kJ mol^{-1}

$\Delta_f H^\circ\{C_6H_6(l)\} = ?$ $\quad \Delta_f H^\circ\{O_2(g)\} = 0$

$\therefore \quad -3267.0 = 6(-393.5) + 3(-285.3) - \Delta_f H^\circ[C_6H_6(l)] - \frac{15}{2}(0)$

$-3267.0 = -2361.0 - 857.49 - \Delta_f H^\circ\{C_6H_6(l)\} - 0$

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$\therefore\ \Delta_f H^o\ \{C_6H_6(l)\} = -2361.0 - 857.49 + 3267.0$

$= \mathbf{48.51\ kJ\ mol^{-1}}$

Standard enthalpy of formation of C_6H_6

$= 48.51\ kJ\ mol^{-1}$

❑ **Example 27.**

Enthalpies of formation of CO(g), CO_2 (g), N_2O(g) and N_2O_4(g) are –110, –393, 81 and 9.7 kJ mol^{-1} respectively. Calculate $\Delta_r H$ for the reaction :

$$N_2O_4(g) + 3CO(g) \longrightarrow N_2O(g) + 3CO_2(g)$$

Solution: $N_2O_4(g) + 3CO(g) \longrightarrow N_2O(g) + 3CO_2(g)$

$\Delta_r H = \Delta_f H\,[N_2O(g)] + 3\Delta_f H\,[CO_2(g)] - \{\Delta_f H[N_2O_4(g)] + 3\Delta_f H\,[CO(g)]\}$

$= 81 + 3 \times (-393) - \{9.7 + 3(-110)\}$

$= 81 - 1179 - 9.7 + 330$

$= -777.7\ kJ\ mol^{-1}$

Practice Problems

13. The enthalpy of formation of $Fe_2O_3(s)$ is $-824.2\ kJ\ mol^{-1}$. Calculate the enthalpy change for the reaction :

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

14. The $\Delta_r H^o$ for the reaction,

$$4S(s) + 6O_2(g) \longrightarrow 4SO_3(g)$$

is -1583.2 kJ. Calculate ΔH_f^o of sulphur trioxide.

15. Calculate $\Delta_f H^o$ for the reaction,

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$$

Given that $\Delta_f H^o$ for $CO_2(g)$, CO(g) and H_2O (g) are -393.5, -111.3 and $-241.8\ kJ\ mol^{-1}$ respectively.

16. The enthalpy of formation of $C_2H_5OH(l)$, $CO_2(g)$ and $H_2O(l)$ are -277.0, -393.5 and -285.8 kJ/mol respectively. Calculate the enthalpy change for the reaction :

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

17. Calculate the standard enthalpy of formation of ethylene, $C_2H_4(g)$ from the following thermochemical equation :

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g) \qquad \Delta_r H^\circ = -1323\ kJ$$

Given the standard enthalpy of formation of CO_2 (g) and $H_2O(g)$ are -393.5 and $-249\ kJ\ mol^{-1}$ respectively.

18. The standard molar enthalpy of formation of ethane, carbon dioxide and liquid water are -21.1, -94.1 and -68.3 kcal respectively. Calculate the standard enthalpy change of the following reaction :

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$$

19. Calculate $\Delta_r H^\circ$ for the reaction :

$$2H_2S(g) + 3O_2(g) \longrightarrow 2H_2O(l) + 2SO_2(g)$$

Given $\Delta_f H^\circ$ values : $H_2S(g) = -20.60$;

$H_2O(l) = -285.83$; $SO_2(g) = -296.83\ kJ\ mol^{-1}$

Answers to Practice Problems

13. –1648.4 kJ **14.** – 395.8 kJ
15. 40.4 kJ **16.** – 1367.4 kJ
17. 38 kJ mol^{-1} **18.** – 744.0 kcal
19. – 1124.12 kJ mol^{-1}

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ENTHALPY OF COMBUSTION

The enthalpy change (or heat change) when 1 mole of a substance is completely burnt in excess of oxygen or air is called **enthalpy of combustion.**

It is generally denoted by $\Delta_c H$. Some examples of combustion reactions are given below :

(*i*) Combustion of carbon

$$C(s) + O_2(g) \longrightarrow CO_2(g); \qquad \Delta H = \Delta_c H = -393.5\ kJ$$

(*ii*) Combustion of methane

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = \Delta_c H = -890.3 kJ$$

(*iii*) Combustion of benzene (C_6H_6)

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l); \qquad \Delta H = \Delta_c H = -3268\ kJ$$

(*iv*) Combustion of ethyl alcohol

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l); \qquad \Delta H = \Delta_c H = -1367.4\ kJ$$

Cooking gas in cylinders contains mostly butane (C_4H_{10}). During complete combustion of one mole of butane 2658 kJ of heat is released.

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l) \qquad \Delta_c H^o = -2658.0\ kJ\ mol^{-1}$$

Similarly, combustion of glucose releases 2802 kJ mol^{-1} of heat.

$$\underset{\text{Glucose}}{C_6H_{12}O_6(s)} + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta_c H^o = -2802\ kJ\ mol^{-1}$$

It may be noted that the enthalpy of combustion ($\Delta_c H^o$) is always **negative** because combustion reactions are always **exothermic** and heat is evolved during combustion. Enthalpy of combustion of some common fuels are given in Table 3.

Efficiency of Fuels and Foods

For the working of machines, fuels such as coal, petroleum and natural gas are needed which undergo combustion with the release of energy. The energy released keeps the machines working. More is the energy released, better is the fuel. Human body is also like a machine which requires some energy to keep it running or working. The food that we eat serves as source of energy to our body. As a result, **food is regarded as a fuel for the body.** Coal, petroleum,

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Table 3. Enthalpy of combustion of some common fuels.

Fuel	Combustion reaction	$\Delta_c H^\circ$ (kJ mol^{-1})
Hydrogen	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	– 286.4
Methane	$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$	– 890.3
Butane	$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$	– 2658.0
Methanol	$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	– 726.5
Octane	$C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(l) + 9H_2O$	– 5460.0
Ethanol	$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$	– 1367.5

natural gas, etc. are regarded as fuels for many machines and industrial processes. Carbohydrates are the major constituents of our food. The carbohydrates are broken to glucose or its derivatives in our body. The glucose burns to give energy to our body. The enthalpy of combustion of glucose ($C_6H_{12}O_6$) is given by

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

Glucose $\quad \Delta H^\circ = -2802$ kJ mol^{-1}

Our body also generates energy from food by the same overall process as combustion reaction. However, the final products are produced after a series of complex biochemical reactions involving enzymes.

This oxidation reaction is called **combustion of food.** The above reaction occurs in several small steps and the temperature does not become excessive as we observe during combustion reaction in a flame. Enzymes act as catalysts and these make the reactions possible at body temperature. The energy released in various oxidation steps results in the formation of energy rich molecules. These energy rich molecules deliver the energy at appropriate sites in our body. The nitrogen present in our food is mainly converted to urea (NH_2CONH_2) which is excreted out in urine.

Calorific value of Foods and Fuels

The energy released by the combustion of foods or fuels is usually compared in terms of their combustion energy per gram. It is known as **calorific value.** It is defined as

the amount of heat produced in calories (or joules) when one gram of a substance (food or fuel) is completely burnt.

The calorific value is usually expressed in kcal per gram or kilojoules per gram (1 kcal = 4.184 kJ). For example, when methane burns, 890.3 kJ mol^{-1} of energy is liberated as

$$CH_4(g) + 2O_2 \longrightarrow CO_2(g) + 2H_2O(l); \quad \Delta_c H = -890.3 \text{ kJ mol}^{-1}$$

Therefore, calorific value of methane is :

$$\text{Heat produced per gram} = \frac{890.3}{16} = 55.6 \text{ kJ}$$

(Molar mass of CH_4 = 16)

Similarly, octane, a component of gasoline burns as :

$$C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l)$$

$$\Delta_c H = -5460 \text{ kJ mol}^{-1}$$

$\therefore$ Calorific value of $C_8H_{18}(l)$ is :

$$\frac{5460}{114} = 47.9 \text{ kJ}$$

(Molar mass of C_8H_{18} = 114)

Calorific values of some important foodstuffs and fuels are given in Table 4.

Table 4. Calorific values of some common fuels and foods.

Substance	Calorific value (kJ/g)
Fuels	
Charcoal	33
Wood	17
Dung cake	6–8
Kerosene	48
Fuel oil	45
Hydrogen	150
Methane	55
Butane (LPG)	55
Foods	
Butter	30.4
Ghee	37.6
Milk	3.2
Curd	2.5
Honey	13.3
Rice	14.5
Egg	7.3
Meat	12.0

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Table 4 shows that out of all the fuels listed, *hydrogen has the highest calorific value*. However, because of some technical problems in holding it safely, it is not commonly used as domestic or industrial fuel.

Among the foods, **fats and carbohydrates are the principal sources of energy which** have high calorific values. Proteins are also the main constituents of foods. On an average, an adult requires 8000 to 12000 kJ of energy per day. This means that the balanced diet of a person must include foodstuffs which provide enough carbohydrates, fats, proteins, oils, vitamins, etc. From the calorific values of different foods, it is possible to calculate the food requirement of an average person for the balanced diet.

SOLVED EXAMPLES

❑ Example 28.

The enthalpies of combustion of CH_4 and C_2H_6 are –890.3 and –1559.7 kJ mol^{-1} respectively. Which of the two has greater efficiency of fuel per gram?

Solution: The fuel efficiency can be predicted from the amount of heat evolved for every gram of fuel consumed.

(*i*) The combustion of methane is as follows :

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta_c H = 890.3 \text{ kJ mol}^{-1}$$

Molar mass of $CH_4 = 16$

$$\therefore \text{ Heat produced per gram } = \frac{890.3}{16} = 55.64 \text{ kJ g}^{-1}$$

(*ii*) The combustion of ethane is as follows :

$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

$$\Delta_c H = -1559.7 \text{ kJ mol}^{-1}$$

Molar mass of $C_2H_6 = 30$

$$\text{Heat produced per gram } = \frac{1559.7}{30} = 51.99 \text{ kJ g}^{-1}$$

Thus, **methane has greater fuel efficiency than ethane.**

❑ Example 29.

In a gobar gas plant, gobar gas is obtained by bacterial fermentation of animal refuse. It is found to contain mainly methane and its heat of combustion given by the equation :

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

is 809 kJ mol^{-1}. How much gobar gas would have to be produced per day for a small village community of 100 families, if we assume that each family has to be supplied 20,000 kJ of energy per day to meet all its needs. The methane content in gobar gas is 80% by weight.

Solution: Energy consumption of one family per day

$$= 20{,}000 \text{ kJ}$$

Total number of families = 100

Energy consumption of 100 families per day

$$= 100 \times 20{,}000 = 2 \times 10^6 \text{ kJ}$$

The combustion of methane present in gobar gas may be written as :

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + 809 \text{ kJ}$$

According to the equation, 809 kJ of energy is evolved from methane

$$= 6 \text{ g}$$

2×10^6 kJ of energy will be evolved from methane

$$= \frac{16}{809} \times 2 \times 10^6 \text{ g}$$

$$= 3.96 \times 10^4 \text{ g} = 39.6 \text{ kg}$$

Since methane content of gobar gas is 80% by weight, therefore,

$$\text{Weight of gobar gas needed} = \frac{39.6 \times 100}{80} = \mathbf{49.5 \text{ kg}}$$

❑ Example 30.

(a) A cylinder of gas supplied by a company is assumed to contain 14 kg of butane. If a normal family requires 20,000 kJ of energy per day for cooking, how long will the cylinder last ?

(b) If the air supplied to the burner is insufficient, a portion of gas escapes without combustion. Assuming that 25% of the gas is wasted due to this inefficiency, how long will the cylinder last? (Heat of combustion of butane = 2658 kJ/mol)

Solution: (*a*) Molecular formula of butane

$$= C_4H_{10}$$

Molecular mass of butane $= 4 \times 12 + 10 \times 1 = 58$

Heat of combustion of butane

$$= 2658 \text{ kJ mol}^{-1}$$

1 mole or 58 g of butane on complete combustion give heat

$$= 2658 \text{ kJ}$$

$\therefore$ 14×10^3 g of butane on complete combustion give heat

$$= \frac{2658 \times 14 \times 10^3}{58}$$

$$= 641586$$

The family needs 20,000 kJ of heat per day

20,000 kJ of heat is used for cooking by a family in = 1 day 641586 kJ of heat will be used for cooking by a family in

$$= \frac{641586}{20000} = \mathbf{32 \text{ days}}$$

The cylinder will last for 32 days

(*b*) 25 per cent of the gas is wasted due to inefficiency. This means that only 75% of butane gets combusted. Therefore,

The energy produced by 75% combustion of butane

$$= \frac{641586 \times 75}{100} = 481190 \text{ kJ}$$

$\therefore$ the number of days the cylinder will last

$$= \frac{481190}{20000} = \mathbf{24 \text{ days}}$$

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Practice Problems

20. The enthalpy of formation of CH_4, C_2H_6 and C_4H_{10} are – 74.8, – 84.7 and – 126.1 kJ mol^{-1} respectively. Arrange them in the order of their efficiency as fuel per gram (enthalpy of formation of $CO_2(g)$ and $H_2O(l)$ are – 393.5 and – 285.8 kJ mol^{-1} respectively).

21. Sucrose undergoes combustion as :

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(l) + 5645 \text{ kJ mol}^{-1}$$

(*i*) How much energy will be liberated when 51.3 g of sucrose is burnt?

(*ii*) What is the energy required for the production of 5.472 g of sucrose ?

22. A cylinder of indane gas contains 11.2 kg of butane. A normal family requires 25000 kJ energy per day for cooking. How long will the cylinder of gas last if the efficiency of combustion is 80%? (Heat of combustion of butane is 2658 kJ mol^{-1}).

23. An intimate mixture of Fe_2O_3 and Al is used in a solid fuel rocket. Calculate the fuel value per gram and fuel value per cc of mixture. Heats of formation and densities are as follows :

$\Delta_f H$ (Al_2O_3) = 399 kcal/mole, $\Delta_f H$ (Fe_2O_3) = 199 kcal/mole

(Density of Fe_2O_3 = 5.2 g/cc. Density of Al = 2.7 g/cc)

Answers to Practice Problems

20. $CH_4 > C_2H_6 > C_4H_{10}$

21. (*i*) 846.75 kJ (*ii*) 90.32 kJ

22. 16.4 days

23. 0.9346 kcal/g, 3.94 kcal/cc.

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HESS'S LAW OF CONSTANT HEAT SUMMATION

In 1840 a Russian chemist G.H. Hess proposed an important generalisation regarding the enthalpies (heats) of reactions known as **Hess's law.** It states that

the enthalpy change (or heat evolved or absorbed) in a particular reaction is the same whether the reaction takes place in one step or in a number of steps.

This means that the amount of heat evolved or absorbed in a chemical reaction depends only upon the enthalpy of initial reactants and the final products irrespective of the path or the manner by which the change has taken place. In other words, ***the standard reaction enthalpy is the sum of the standard enthalpies of the reactions into which the overall reaction may be divided at the same temperature*** **split up. This is consistent with the fact that enthalpy is a state function.** Suppose in a reaction, the reactant A changes to product B in one step and the enthalpy change during this process is ΔH. Now suppose the same process is carried out in two steps (Fig. 13).

(*i*) The reactant A changes to C (intermediate stage) and the enthalpy change during this step is ΔH_1.

(*ii*) C changes to the product B and the enthalpy change during this step is ΔH_2.

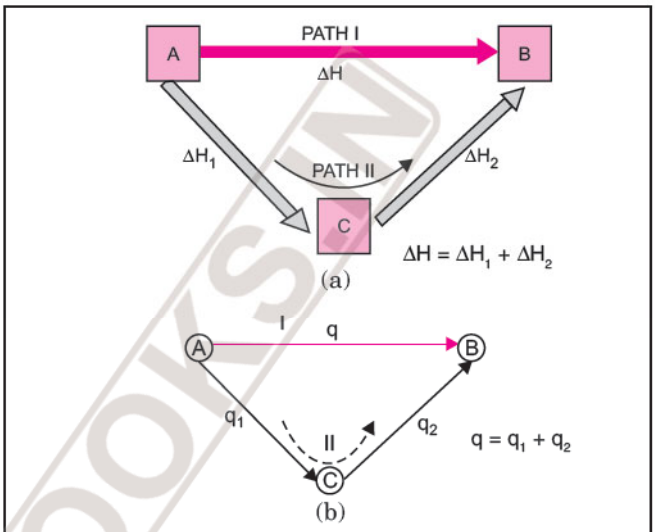

Fig. 13. Illustration of Hess's law.

Thus, according to Hess's law, the enthalpy change for the reaction, whether the reaction follows path I or path II is :

$$\Delta H = \Delta H_1 + \Delta H_2$$

Thus, in general, if enthalpy of an overall reaction A ⟶ B along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$..... represent enthalpies of reactions leading to the same product B along another route , then Hess's law of heat summation may be represented as

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 + ...$$

Theoretical justification of the Hess's Law. The theoretical justification can be obtained from the following considerations :

The substance A can be converted into B by two paths [Fig. 13 (*b*)]. In path I, A is converted directly into B and let heat evolved in this step be q. On the other hand, when path II is followed, let the heats evolved during the two steps A to C and C to B be q_1 and q_2 respectively. The total heat evolved in path II is $q' = q_1 + q_2$. According to Hess's law, q' must be equal to q.

Let us suppose that q' is greater than q. This means that by converting A to B by path II and then converting B back to A by path I, the heat energy equal to $q' - q$ can be created. This directly comes in conflict with the law of conservation of energy (first law of thermodynamics), according to which the energy can neither be created nor destroyed. Hence, q must be equal to q'. In other words, heat changes during the process must be independent of the path. This is Hess's law.

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Illustration of Hess's Law. Let us illustrate the law by considering the formation of carbon dioxide from carbon and oxygen. Carbon can be converted into CO_2 by two ways :

Path 1. $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\circ = -393.5$ kJ

Path 2. $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$; $\Delta_r H_1^\circ = -110.5$ kJ

$CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H_2^\circ = -283.0$ kJ

$C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\circ = -393.5$ kJ

$\therefore \quad \Delta H = \Delta H_1 + \Delta H_2$

This is also shown diagrammatically in Fig. 14.

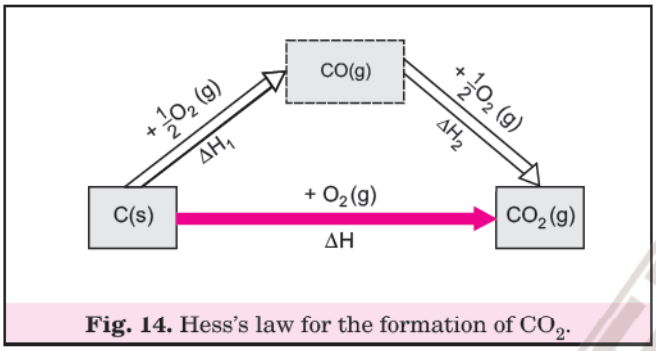

Fig. 14. Hess's law for the formation of CO_2.

Hence, it may be concluded that according to Hess's law,

the thermochemical equations can be added, subtracted or multiplied like algebraic equations to obtain the desired equation.

Applications of Hess's Law

Hess's law has been found to be very useful in determining the enthalpy changes for the chemical reactions which are not suitable for direct measurements with calorimeter. Therefore, it has many applications in the study of chemical energetics. Some of the important applications of Hess's law are :

1. Determination of enthalpy of formation of substances which cannot be measured experimentally.

There are a large number of compounds such as methane (CH_4), carbon monoxide (CO), benzene (C_6H_6), etc. which cannot be synthesised directly from their elements. Therefore, their enthalpies of formation cannot be determined experimentally by calorimetric method. The enthalpies of formation of such substances can be determined by an *indirect method* based on Hess's law.

For example, enthalpy of formation of carbon monoxide can be calculated from the enthalpy of combustion data for carbon and carbon monoxide.

(*i*) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\circ = -393.5$ kJ

(*ii*) $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\circ = -283.0$ kJ

By subtracting eq. (*ii*) from eq (*i*), we get

$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$; $\Delta_r H^\circ = -110.5$ kJ

Thus, the enthalpy of formation of carbon monoxide is –110.5 kJ which has been obtained indirectly from the experimentally determined enthalpy of combustion values of C(*s*) and CO(*g*).

❑ Example 31.

Calculate the enthalpy of formation of ethane from the following data :

(*i*) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\circ = -393.5$ kJ

(*ii*) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$; $\Delta_r H^\circ = -285.8$ kJ

(*iii*) $C_2H_6(g) + \frac{7}{2} O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$; $\Delta_r H^\circ = -1560.0$ kJ

Solution: The required equation for the formation of ethane is :

$2C(s) + 3H_2(g) \longrightarrow C_2H_6(g)$; $\Delta_r H^\circ = ?$

Multiply eq. (*i*) by 2 and eq. (*ii*) by 3 and add

(*i*) × 2 $2C(s) + 2O_2(g) \longrightarrow 2CO_2(g)$; $\Delta_r H^\circ = -787.0$ kJ

(*ii*) × 3 $3H_2(g) + \frac{3}{2} O_2(g) \longrightarrow 3H_2O(l)$; $\Delta_r H^\circ = -857.4$ kJ

Adding

(*iv*) $2C(s) + 3H_2(g) + \frac{7}{2} O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$ $\Delta_r H^\circ = -1644.4$ kJ

Subtract eq. (*iii*) from the above eq. (*iv*)

(*iv*) $C_2H_6(g) + \frac{7}{2} O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$; $\Delta_r H^\circ = -1560.0$ kJ

Subtracting $2C(s) + 3H_2(g) \longrightarrow C_2H_6(g)$; $\Delta_r H^\circ = -84.4$ kJ

Thus, enthalpy of formation of ethane = **– 84.4 kJ**

❑ Example 32.

Calculate the standard enthalpy of formation of CH_3OH (l) from the following data :

$CH_3OH(l) + \frac{3}{2} O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$\Delta_r H^\circ = -726$ kJ mol^{-1}

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$C(s) + O_2(g) \longrightarrow CO_2(g)\ \Delta_r H^\circ = -393\ kJmol^{-1}$

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)\ \Delta_r H^\circ = -286.0\ kJ\ mol^{-1}$

N.C.E.R.T.

Solution: The required equation for the formation of $CH_3OH(l)$ is :

$$C(s) + 2H_2(g) + \frac{1}{2} O_2(g) \longrightarrow CH_3OH(l)$$

The given equations are :

$$(i)\ CH_3OH(l) + \frac{3}{2} O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$\Delta_r H^\circ = -726\ kJmol^{-1}$

$$(ii)\ C(s) + O_2(g) \longrightarrow CO_2(g)$$

$\Delta_r H^\circ = -393\ kJ\ mol^{-1}$

$$(iii)\ H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$$

$\Delta_r H^\circ = -286.0\ kJmol^{-1}$

Multiply eq. (*iii*) by 2 and add to eq. (*ii*)

$$(ii)\ C(s) + O_2(g) \longrightarrow CO_2(g)$$

$\Delta_r H^\circ = -393\ kJ\ mol^{-1}$

$$(iii) \times 2\quad 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

$\Delta_r H^\circ = -572\ kJ\ mol^{-1}$

Adding (*i*) and (*iii*) we get

$$(iv)\ C(s) + 2H_2(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$\Delta_r H^\circ = -965\ kJ\ mol^{-1}$

Subtract *eq.* (*i*) from *eq* (*iv*)

$$(i)\ CH_3OH(l) + \frac{3}{2} O_2(g) \longrightarrow CO_2 + 2H_2O(l)$$

$\Delta_r H^\circ = -726\ kJ\ mol^{-1}$

$$C(s) + 2H_2(g) + \frac{1}{2} O_2(g) \longrightarrow CH_3OH(l)$$

$\Delta_r H^\circ = \mathbf{-239\ kJ}\ mol^{-1}$

Example 33.

Calculate the enthalpy of formation of benzene represented by the following reaction :

$$6C(s) + 3H_2(g) \longrightarrow C_6H_6(l)$$

The standard enthalpy of combustion of benzene is –3266.0 kJ and standard enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are – 393.1 and – 286.0 kJ respectively.

Solution: The required equation is :

$$(i)\quad 6C(s) + 3H_2(g) \longrightarrow C_6H_6(l);\quad \Delta_f H^\circ = ?$$

Other equations representing various reactions can be written as

$$(ii)\quad C_6H_6(l) + 7\frac{1}{2} O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$$

$\Delta_r H^\circ = -3266.0$ kJ

$$(iii)\quad C(s) + O_2(g) \longrightarrow CO_2(g);$$

$\Delta_r H^\circ = -393.1$ kJ

$$(iv)\quad H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l);$$

$\Delta_r H^\circ = -286.0$ kJ

Multiply eq. (*iii*) by 6 and eq. (*iv*) by 3 and add

$$(iii) \times 6\quad 6C(s) + 6O_2(g) \longrightarrow 6CO_2(g);$$

$\Delta_r H^\circ = -2358.6$ kJ

$$(iv) \times 3\quad 3H_2(g) + \frac{3}{2} O_2(g) \longrightarrow 3H_2O(l);$$

$\Delta_r H^\circ = -858.0$ kJ

Adding

$$(v)\ 6C(s) + 3H_2(g) + \frac{15}{2} O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l);$$

$\Delta_r H^\circ = -3216.6$ kJ

Subtract eq. (*ii*) from eq. (*v*)

$$(vi)\quad C_6H_6(l) + \frac{15}{2} O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l);$$

$\Delta_r H^\circ = -3266.0$ kJ

Subtracting $6C(s) + 3H_2(g) \longrightarrow C_6H_6(l)$;

$\Delta_r H^\circ = +49.6$ kJ

$\therefore$ Enthalpy of formation of benzene = **+ 49.6 kJ**

Example 34.

Calculate the $\Delta_r H^0$ at 298 K for the reaction :

$$C\ (graphite) + 2H_2(g) \longrightarrow CH_4(g)$$

from the following data :

$$C\ (graphite) + O_2(g) \longrightarrow CO_2\ (g)$$

$\Delta_r H^\circ = -393.5\ kJ\ mol^{-1}$

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$$

$\Delta_r H^\circ = -285.8\ kJ\ mol^{-1}$

$$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g)$$

$\Delta_r H^\circ = +890.3\ kJ\ mol^{-1}$

Solution: The required equation is

$$(i)\quad C\ (graphite) + 2H_2(g) \longrightarrow CH_4(g)\quad \Delta_r H^0 = ?$$

Other equations given are :

$$(ii)\quad C\ (graphite) + O_2(g) \longrightarrow CO_2(g)$$

$\Delta_r H^\circ = -393.5$ kJ mol^{-1}

$$(iii)\quad H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$$

$\Delta_r H^\circ = -285.8$ kJ mol^{-1}

$$(iv)\quad CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g)$$

$\Delta_r H^\circ = +890.3$ kJ mol^{-1}

Multiply eqn. (*iii*) by 2 and add to eqn. (*ii*)

$$(ii)\quad C\ (graphite) + O_2(g) \longrightarrow CO_2(g)$$

$\Delta_r H^\circ = -393.5$ kJ mol^{-1}

$$(iii) \times 2\quad 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

$\Delta_r H^\circ = -571.6$ kJ mol^{-1}

Adding

$$(v)\ C\ (graphite) + 2H_2(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$\Delta_r H^\circ = -965.1$ kJ mol^{-1}

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Add eqn. *(iv)* to *(v)*

(iv) $CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g)$

$\Delta_r H^\circ = +890.3 \text{ kJ mol}^{-1}$

Adding

$C \text{ (graphite)} + 2H_2(g) \longrightarrow CH_4(g)$

$\Delta_r H^\circ = \mathbf{-74.8 \text{ kJ mol}^{-1}}$

Practice Problems

24. Calculate the enthalpy of formation of acetic acid (CH_3COOH) if its enthalpy of combustion is -867 kJ mol^{-1}. The enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are -393.5 and $-285.9 \text{ kJ mol}^{-1}$ respectively.

25. Calculate the standard enthalpy of formation of propane (C_3H_8) if its enthalpy of combustion is $-2220.2 \text{ kJ mol}^{-1}$. The enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ ar -393.5 and $-285.8 \text{ kJ mol}^{-1}$ respectively.

26. Calculate the enthalpy of formation of ethyl alcohol from the following data :

$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$; $\Delta_r H^\circ = -1368.0$ kJ

$C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\circ = -393.5$ kJ

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$; $\Delta_r H^\circ = -286.0$ kJ

27. Calculate the enthalpy of formation of methane from the following data :

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta_r H^\circ = -393.5$ kJ

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ $\Delta_r H^\circ = -571.8$ kJ

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ $\Delta_r H^\circ = -890.3$ kJ

Answers to Practice Problems

24. $-491.8 \text{ kJ mol}^{-1}$

25. $-103.5 \text{ kJ mol}^{-1}$

26. $-277.0 \text{ kJ mol}^{-1}$

27. $-75.0 \text{ kJ mol}^{-1}$

Hints & Solutions on page 78

2. Determination of enthalpy of transition.

Hess's law is useful in determining the enthalpies of transition of the allotropic modifications such as graphite to diamond, rhombic sulphur to monoclinic sulphur, yellow phosphorus to red phosphorus, etc.

For example, the enthalpies of combustion of diamond and graphite have been found to be -395.4 kJ and -393.5 kJ respectively. The enthalpy of transition of allotropic transformation from diamond to graphite can be calculated with the help of Hess's law.

The enthalpies of combustion can be represented as :

(i) $C \text{ (diamond)} + O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\circ = -395.4$ kJ

(ii) $C \text{ (graphite)} + O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\circ = -393.5$ kJ

The conversion can be written as :

$C \text{ (diamond)} \longrightarrow C \text{ (graphite)}$ $\Delta_r H^\circ = ?$

This can be obtained by subtracting eq. *(ii)* from eq. *(i)*

(i) $C \text{ (diamond)} + O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\circ = -395.4$ kJ

(ii) $C \text{ (graphite)} + O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\circ = -393.5$ kJ

Subtracting

$C \text{ (diamond)} \longrightarrow C \text{(graphite)}$; $\Delta_r H^\circ = -1.9$ kJ

Practice Problems

28. Calculate the enthalpy of allotropic transformation from monoclinic to rhombic sulphur from the following data :

$S(\text{rhombic}) + O_2(g) \longrightarrow SO_2(g)$ $\Delta_r H^\circ = -294.1$ kJ

$S(\text{monoclinic}) + O_2(g) \longrightarrow SO_2(g)$ $\Delta_r H^\circ = -295.4$ kJ

28. -1.3 kJ

Hints & Solutions on page 78

3. Calculation of enthalpy of hydration.

Hess's law is also useful in calculating the enthalpies of hydration of substances. The **enthalpy of hydration** is defined as

the enthalpy change (heat evolved or absorbed) when one mole of the anhydrous salt combines with the required number of moles of water to form hydrated salt.

For example, the enthalpy of hydration of copper sulphate is -78.2 kJ. This may be represented as :

$CuSO_4(s) + 5H_2O \longrightarrow CuSO_4 . 5H_2O(s)$; $\Delta_r H^\circ = -78.2$ kJ

This can be calculated from the enthalpies of solution of anhydrous and hydrated salts as illustrated ahead :

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❑ **Example 35.**

The enthalpies of solution of anhydrous $CuSO_4$ and hydrated $CuSO_4 .5H_2O$ are –66.5 and 11.7 kJ mol^{-1} respectively. Calculate the enthalpy of hydration of $CuSO_4$ to $CuSO_4 . 5H_2O$.

Solution: The required equation is :

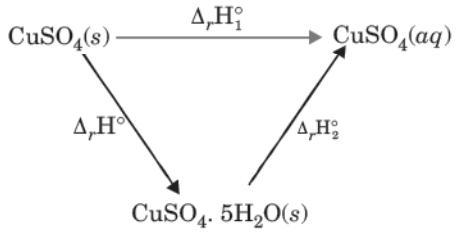
$$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4 . 5H_2O(s) \qquad \Delta_r H = ?$$

given that

$$CuSO_4(s) + aq \longrightarrow CuSO_4(aq) \qquad \Delta_r H_1^\circ = -66.5 \text{ kJ}$$

$$CuSO_4.5H_2O(s) + aq \longrightarrow CuSO_4(aq) \qquad \Delta_r H_2^\circ = +11.7 \text{ kJ}$$

The process of hydration may be expressed as



According to Hess's law

$$\Delta_r H_1^\circ = \Delta_r H^\circ + \Delta_r H_2^\circ$$

$$\Delta_r H^\circ = \Delta_r H_1^\circ - \Delta_r H_2^\circ$$

$$= -66.5 - 11.7 = \mathbf{-78.2 \text{ kJ}}$$

Practice Problems

29. Enthalpies of solution of $BaCl_2.2H_2O$ and $BaCl_2$ are 8.8 and –20.6 kJ mol^{-1} respectively. Calculate the heat of hydration of $BaCl_2$ to $BaCl_2.2H_2O$

29. –29.4 kJ

Hints & Solutions on page 78

4. Predicting enthalpies of various reactions.

Hess's law is useful to calculate enthalpies of many reactions whose direct measurement would be difficult or even quite impossible.

SOLVED EXAMPLES

❑ **Example 36.**

Calculate the enthalpy of formation of anhydrous aluminium chloride, Al_2Cl_6 from the following data :

(i) $2Al(s) + 6HCl\ (aq) \longrightarrow Al_2Cl_6(aq) + 3H_2(g);$ $\Delta_r H^\circ = -1004.0$ kJ

(ii) $H_2(g) + Cl_2\ (aq) \longrightarrow 2HCl(g);$ $\Delta_r H^\circ = -183.9$ kJ

(iii) $HCl(g) + aq \longrightarrow HCl(aq);$ $\Delta_r H^\circ = -73.2$ kJ

(iv) $Al_2Cl_6(s) + aq \longrightarrow Al_2Cl_6(aq);$ $\Delta_r H^\circ = -643.0$ kJ

Solution: *(i)* The formation of Al_2Cl_6 from its elements may be represented as :

$$2Al(s) + 3Cl_2(g) \longrightarrow Al_2Cl_6(s); \qquad \Delta_f H^\circ = ?$$

Multiply eq. *(ii)* by 3 and eq. *(iii)* by 6 and add

(ii) × 3 $3H_2(g) + 3Cl_2(g) \longrightarrow 6HCl(g);$ $\Delta_r H^\circ = -551.7$ kJ

(iii) × 6 $6HCl(g) + aq \longrightarrow 6HCl(aq);$ $\Delta_r H^\circ = -439.2$ kJ

Adding

(v) $3H_2(g) + 3Cl_2(g) + aq \longrightarrow 6HCl(aq);$ $\Delta_r H^\circ = -990.9$ kJ

Add. eq. *(i)* to eq. *(v)*

(i) $2Al(s) + 6HCl(aq) \longrightarrow Al_2Cl_6(aq) + 3H_2(g);$ $\Delta_r H^\circ = -1004.0$ kJ

Adding *(vi)* $2Al(s) + 3Cl_2(g) + aq \longrightarrow Al_2Cl_6(aq);$ $\Delta_r H^\circ = -1994.9$ kJ

Subtracting eq. *(iv)* from eq. *(vi)*

(iv) $Al_2Cl_6(s) + aq \longrightarrow Al_2Cl_6(aq);\ \Delta_r H^\circ = -643.0$ kJ

Subtracting

$$2Al(s) + 3Cl_2(g) \longrightarrow Al_2Cl_6(s); \qquad \Delta_r H^\circ = -1351.9 \text{ kJ}$$

Thus, enthalpy of formation of anhydrous Al_2Cl_6 = **–1351.9 kJ**

❑ **Example 37.**

The standard enthalpies of formation of SO_2 (g) and SO_3 (g) are – 296.6 kJ and –395.6 kJ respectively. Calculate ΔH° for the reaction :

$$SO_2(g) + \frac{1}{2} O_2(g) \longrightarrow SO_3(g)$$

Solution: The given equations are :

(i) $S(s) + O_2(g) \longrightarrow SO_2(g);$ $\Delta_r H^\circ = -296.6$ kJ

(ii) $S(s) + \frac{3}{2}O_2(g) \longrightarrow SO_3(g);$ $\Delta_r H^\circ = -395.6$ kJ

The required equation is :

$$SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g); \qquad \Delta_r H^\circ = ?$$

Subtract eq. *(i)* from eq. *(ii)*

(i) $S(s) + \frac{3}{2}O_2(g) \longrightarrow SO_3(g);$ $\Delta_r H^\circ = -395.6$ kJ

(ii) $S(s) + O_2(g) \longrightarrow SO_2(g);$ $\Delta_r H^\circ = -296.6$ kJ

Subtracting $SO_2(s) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g);$ $\Delta_r H^\circ = \mathbf{-99.0}$ kJ

❑ **Example 38.**

Calculate the standard enthalpy of formation of carbon disulphide (l). Given that the standard

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enthalpies of combustion of carbon (s), sulphur (s) and carbon disulphide (l) are –393.3, –293.72 and –1108.76 kJ mol^{-1} respectively.

Solution: The given equations are :

(*i*) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\circ = -393.3$ kJ

(*ii*) $S(s) + O_2(g) \longrightarrow SO_2(g)$; $\Delta_r H^\circ = -293.72$ kJ

(*iii*) $CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$; $\Delta_r H^\circ = -1108.76$ kJ

The required equation is

$C(s) + 2S(g) \longrightarrow CS_2(l)$; $\Delta_r H^\circ = ?$

Multiply eq. (*ii*) by 2 and add to eq. (*i*)

(*i*) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\circ = -393.3$ kJ

(*ii*) × 2 $2S(s) + 2O_2(g) \longrightarrow 2SO_2(g)$; $\Delta_r H^\circ = -587.44$ kJ

Adding $C(s) + 2S(s) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$; $\Delta_r H^\circ = -980.74$ kJ

Subtract eq. (*iii*)

(*iii*) $CS_2(l) + 3O_2(s) \longrightarrow CO_2(g) + 2SO_2(g)$; $\Delta_r H^\circ = -1108.76$ kJ

Subtracting $C(s) + 2S(s) \longrightarrow CS_2(l)$; $\Delta_r H^\circ = \mathbf{+128.02}$ **kJ**

Practice Problems

30. The enthalpies of combustion of $C_2H_4(g)$, $C_2H_6(g)$ and H_2 are – 1409.5 kJ, –1558.3 kJ and – 285.6 kJ, respectively. Calculate the enthalpy of hydrogenation of ethylene.

31. Calculate the enthalpy of formation of KOH (*s*) from the following data :

$K(s) + H_2O(l) + (aq) \longrightarrow KOH(aq) + \frac{1}{2} H_2(g)$; $\Delta_r H^\circ = -200.8$ kJ

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$; $\Delta_r H^\circ = -286.3$ kJ

$KOH(s) + (aq) \longrightarrow KOH(aq)$; $\Delta_r H^\circ = -58.6$ kJ

32. The combustion of butane (C_4H_{10}) is exothermic by 2878.7 kJ mol^{-1}. Calculate the standard enthalpy of formation of butane given that the standard enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are – 393.5 kJ mol^{-1} and –285.8 kJ mol^{-1} respectively.

33. Calculate the enthalpy of combustion of nitric oxide (NO) from the following data :

$\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \longrightarrow NO(g)$; $\Delta_r H^\circ = 90.7$ kJ

$\frac{1}{2} N_2(g) + O_2(g) \longrightarrow NO_2(g)$; $\Delta_r H^\circ = 34.0$ kJ

34. The molar enthalpies of combustion of $C_2H_2(g)$, C (graphite) and H_2 (*g*) are – 310.62 kcal, – 94.05 kcal and – 68.32 kcal respectively. Calculate the standard enthalpy of formation of $C_2H_2(g)$.

Answers to Practice Problems

30. –136.8 kJ mol^{-1} **31.** – 428.5 kJ mol^{-1}

32. –122.8 kJ mol^{-1} **33.** – 56.7 kJ mol^{-1}

34. 54.20 kcal

Hints & Solutions on page 78

OTHER TYPES OF ENTHALPIES

In addition to enthalpy of formation and enthalpy of combustion, there are some other types of enthalpies such as enthalpy of solution, enthalpy of neutralisation, enthalpy of phase transition etc. These are discussed below :

ENTHALPY OF SOLUTION

The dissolution of a substance in a solvent is accompanied by an enthalpy change called the enthalpy of solution.

Enthalpy of solution of a substance is the **enthalpy change when one mole of it dissolves in a specified amount of solvent at a constant temperature and pressure.**

For example, the enthalpy change for dissolving one mole of gaseous hydrogen chloride in 10 mol of water can be represented by the following equation :

$HCl(g) + 10\ aq \longrightarrow HCl.10\ aq$; $\Delta H = -69.01$ kJ mol^{-1}

For convenience we may use the symbol *aq.* for water.

It may be noted that as more and more water (solvent) is added, more and more amount of heat is produced. Finally, a stage is approached at which enthalpy of solution does not change on the addition of more water. This is called **enthalpy of solution at infinite dilution**. This may be represented as:

$HCl(g) + aq. \longrightarrow HCl(aq)$; $\Delta H = -74.58$ kJ mol^{-1}

Thus, the **enthalpy of solution at infinite dilution is**

the enthalpy change accompanying the dissolution of one mole of a solute in a large excess of solvent so that further addition of the solvent does not produce any further enthalpy change.

At infinte dilution, the interactions between the ions (or solute molecules) become negligible. Some other examples are :

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(*i*) Dissolution of ammonium chloride,

$NH_4Cl\,(s) + aq \longrightarrow NH_4Cl(aq)$

$\Delta H = 16.4\ kJ\ mol^{-1}$

(*ii*) Dissolution of sodium chloride

$NaCl\,(s) + aq \longrightarrow NaCl(aq)\ \Delta H = 5.35\ kJ\ mol^{-1}$

It is very interesting to note that the salts which do not form hydrates dissolve in water with the absorption of heat *i.e.,* ΔH_{soln} is positive. The hydrated salts also dissolve in water with the absorption of heat (ΔH = + ve). However, the anhydrous salts, which form hydrates dissolve in water with the evolution of heat and ΔH_{soln} for these salts are negative. For example ΔH_{soln} for copper sulphate ($CuSO_4$) is negative (ΔH_{soln} = – 66.5 kJ mol^{-1}) whereas that of hydrated copper sulphate ($CuSO_4.5H_2O$) is positive (ΔH_{soln} = 11.7 kJ mol^{-1}). The enthalpy of solution of some common salts at 298 K are given in Table 5.

Table 5. Enthalpy of solution of some salts at 298 K.

Substance	ΔH_{soln} (kJ mol^{-1})
NaCl	+3.9
KCl	+17.2
KBr	+19.9
NaBr	– 0.6
LiBr	–48.8
NaOH	–44.5
KOH	–57.6
Na_2CO_3	–26.7
K_2CO_3	–30.9
NH_4NO_3	+ 25.7
KNO_3	+ 34.9
$NaNO_3$	+ 20.4
K_2SO_4	+ 23.8
$CaCl_2$	– 81.3
$CuSO_4$	– 66.5
$CuSO_4.5H_2O$	11.7
HBr	–83.4
$Ca(NO_3)_2$	–19.2

When an ionic compound dissolves in a solvent, the ions leave the ordered arrangement of ions in the crystal lattice. These become free in solution. These ions get solvated or hydrated (in case solvent is water). The dissolution process may be thought in the following steps :

(*i*) The ionic solid breaks up to form ions in the gaseous state. The enthalpy change of this process when an ionic solid splits up into ions in gaseous state is lattice enthalpy, $\Delta_{lattice}\ H°$.

For example, for a salt AB, lattice enthalpy is the enthalpy change for the process :

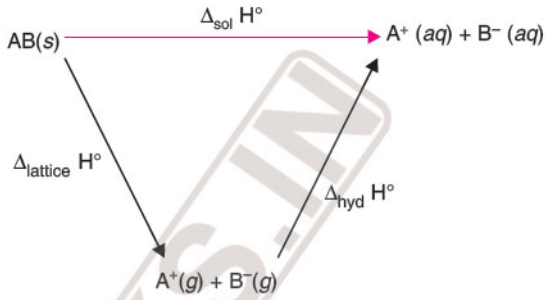
$AB\,(s) \longrightarrow A^+\,(g) + B^-\,(g)\ ;\ \Delta H = \Delta_{lattice}\ H°$

(*ii*) In the second step, heat is released when ions get solvated (or hydrated) by solvent molecules. The enthalpy change of this process when the gaseous ions get solvated (or hydrated) is called **hydration enthalpy,** $\Delta_{hyd}\ H°$. For example, for A^+ and B^- ions,

$A^+(g) + B^-(g) + nH_2O(l) \longrightarrow A^+(aq) + B^-(aq)$

$\Delta H = \Delta_{hyd} H°$

The two processes may be shown as :



The enthalpy of solution of AB(*s*) is therefore determined by the values of the lattice enthalpy, $\Delta_{lattice}\ H$ and enthalpy of hydration, $\Delta_{hyd}\ H$ as :

$\Delta_{sol}\ H° = \Delta_{lattice}\ H° + \Delta_{hyd} H°$

Thus, enthalpies of solution in dilute solution can be expressed as the sum of the lattice enthalpy and enthalpy of hydration of a compound.

For most of the ionic compounds $\Delta_{sol}H$ is positive and therefore, dissolution process is endothermic. Therefore, the solubility of most of salts in water increases with rise in temperature. The solubility of a compound can be decided on the basis of lattice enthalpy and enthalpy of hydration.

If the lattice enthalpy is very high, the dissolution of the compound may not occur at all. This is the reason that fluorides are generally less soluble than corresponding chlorides.

This can also explain easily as to why alkali metal salt say Na_2SO_4 is soluble in water whereas alkaline earth metal salt, $BaSO_4$ is insoluble. The lattice enthalpy of Na_2SO_4 is less than the hydration enthalpy whereas the lattice enthalpy of $BaSO_4$ (because of bivalent charge) is very high so that hydration enthalpy released is not sufficient to break the lattice and it remains insoluble.

Lattice enthalpy

The lattice enthalpy of a compound can be calculated from other thermodynamic properties with the help of a enthalpy diagram called **Born Haber cycle.** Let us discuss this for calculation of lattice enthalpy of sodium chloride [$Na^+\ Cl^-\ (s)$].

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state, *i.e.,*

$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)\ \Delta_{lattice}H°$

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The overall process is thought to take place in the following steps :

(i) Conversion of metallic sodium into gaseous sodium atoms. The sodium atom can lose its electron only in the gaseous state and has to be sublimated. The energy required for the conversion of one mole of metallic sodium into gaseous sodium is called **enthalpy of sublimation.**

$$Na(s) \longrightarrow Na(g)\ ;\ \Delta_{sub}H^\circ = 108.4\ kJ\ mol^{-1}$$

(ii) Dissociation of chlorine molecules into chlorine atoms. Each chlorine molecule consists of two atoms of chlorine. The amount of enthalpy required for the conversion of gaseous chlorine molecule into atoms, is known as **enthalpy of dissociation or enthalpy of atomization, $\Delta_a H^\circ$**

$$Cl_2(g) \longrightarrow 2Cl(g);$$
$$1\ mole \qquad 2\ mole$$

Thus, the enthalpy required for producing one mole of gaseous chlorine atoms is

$$\frac{1}{2}\ Cl_2(g) \longrightarrow Cl(g);\ \Delta_a H^\circ = \frac{242}{2} = 121\ kJ\ mol^{-1}$$

(iii) Conversion of gaseous sodium atoms into sodium ions. The amount of enthalpy required to convert one mole of gaseous sodium atoms into sodium ions in the gaseous state is called **ionisation enthalpy, $\Delta_i H^\circ$.**

$$Na(g) \longrightarrow Na^+(g) + e^-(g) \quad \Delta_i H^o = 495.6\ kJ\ mol^{-1}$$

(iv) Conversion of gaseous chlorine atoms into gaseous chloride ions. The amount of enthalpy released during the conversion of one mole of gaseous chlorine atoms into chloride ions is known as **electron gain enthalpy.**

$$Cl(g) + e^- \longrightarrow Cl^-(g) \quad \Delta_{eg}H^\circ = -348.6\ kJ\ mol^{-1}$$

(v) Combination of oppositely charged ions to form a solid crystal. The oppositely charged Na^+ and Cl^- ions attract each other to form solid NaCl crystal. This leads to the release of energy. The amount of energy released when one mole of solid crystalline compound is obtained from gaseous ions of opposite charges is called lattice enthalpy. It is denoted by **'U'** or **$\Delta_{lattice}\ H^\circ$.**

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)\ \Delta_{lattice}H^\circ$$

The overall energy change may be expressed as :

$$Na\ (s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)\ \Delta_f H^\circ = -411.2\ kJmol^{-1}$$

The enthalpy change for this reaction is called enthalpy of formation and it may be denoted as $\Delta_f H^\circ$.

The various steps may be represented in the form of Born-Haber cycle as shown in Fig. 15.

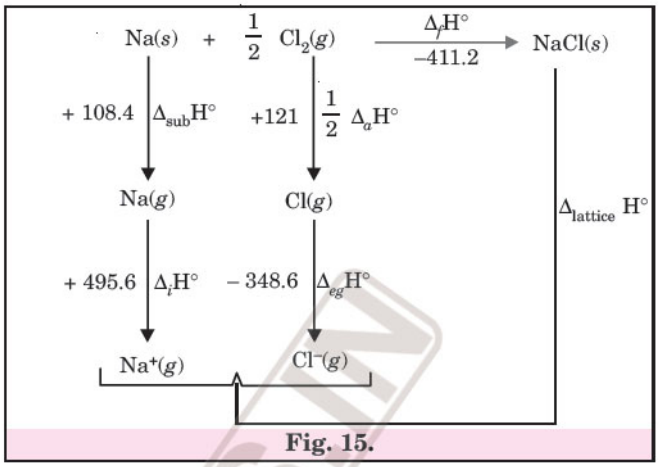

Fig. 15.

* All values are in kJ mol^{-1}.

According to Hess's law, the enthalpy of formation of one mole of sodium chloride should be the same irrespective of the fact whether it takes place directly in one step or through a number of steps as shown above. Thus,

$$\Delta_f H^\circ = \Delta_{sub}H^\circ + \Delta_i H^\circ + \frac{1}{2}\Delta_a H^\circ + \Delta_{eg}H^\circ + \Delta_{lattice}H^\circ$$

Thus, lattice enthalpy can be calculated by knowing the values of different quantities. While using the above relation for lattice enthalpy, **a special care should be taken for the signs of various quantities.** *Positive sign is used for enthalpies absorbed and negative sign is used for enthalpies released.* For NaCl, the various values are :

$$-411.2 = 108.4 + 121 + 495.6 - 348.6 + \Delta_{lattice}H^\circ$$
$$\therefore\ \Delta_{lattice}H^\circ = -411.2 - 108.4 - 121 - 495.6 + 348.6$$
$$= -\ 787.6\ kJ$$

Alternatively, 787.6kJ energy is required to dissociate 1 mole of NaCl i.e.,

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$$
$$\Delta_{lattice}H^\circ = 787.6 kJ\ mol^{-1}$$

Now, enthalpy of solution can be calculated from lattice enthalpy and enthalpy of hydration. The enthalpy of hydration has been found to be $-784.1 kJ\ mol^{-1}$.

Thus

$$\Delta_{sol}H^\circ = +787.6\ kJ\ mol^{-1} - 784.1\ kJ\ mol^{-1}$$
$$= +3.5\ kJ\ mol^{-1}$$

Thus, dissolution of sodium chloride is accompanied by very small heat change.

SOLVED EXAMPLES

❑ Example 39.

Calculate $\Delta_f H^\circ$ for chloride ion from the following data :

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$$
$$\Delta_f H^\circ = -92.8 kJ\ mol^{-1}$$

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$HCl(g) + H_2O \longrightarrow H_3O^+(aq) + Cl^-(aq)$

$\Delta_{diss} H^\circ = -75.2$ kJ mol^{-1} **N.C.E.R.T.**

Solution: (*i*) $\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \longrightarrow HCl(g)$

$\Delta_f H^\circ = -92.8$ kJmol^{-1}

(*ii*) $HCl(g) + H_2O \longrightarrow H_3O^+(aq) + Cl^-(aq)$

$= \Delta_{diss} H^\circ = -75.2$ kJ mol^{-1}

Adding *eq.* (*i*) and (*ii*)

$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) + H_2O \longrightarrow H_3O^+(aq) + Cl^-(aq)$

$\Delta H^\circ = -168.0$ kJ mol^{-1}

$\Delta H = \Delta_f H^\circ(H_3O^+) + \Delta_f H^\circ(Cl^-) - \left[\frac{1}{2}\Delta_f H^\circ(H_2) + \frac{1}{2}\Delta_f H^\circ(Cl_2)\right]$

The enthalpy of formation of H_3O^+ (*aq*) in dilute solution may be taken as zero *i.e.*,

$\Delta_f H^\circ [H_3O^+(aq)] = 0$

$-168.0 = 0 + \Delta_f H^\circ(Cl^-) - \left[\frac{1}{2} \times 0 + \frac{1}{2} \times 0\right]$

$\Delta_f H^\circ(Cl^-) = -168$ kJ mol^{-1}

❑ **Example 40.**

Calculate ΔH for the process at 25°C of dissolving 1.0 mol of KCl in a large excess of water. Does this process represent ionization reaction ? Explain.

$\Delta_f H^\circ [K^+(aq)] = -251.2$ kJ mol^{-1}

$\Delta_f H^\circ [Cl^-(aq)] = -167.08$ kJmol^{-1}

$\Delta_f H^\circ [KCl] = -437.6$ kJ mol^{-1}

Solution: $KCl(s) + nH_2O \longrightarrow K^+(aq) + Cl^-(aq)$

$\Delta H^\circ = \Delta_f H^\circ [K^+(aq)] + \Delta_f H^\circ [Cl^-(aq)] - \Delta_f H^\circ [KCl(s)]$

$= -251.2 + (-167.08) - (-437.6)$

$= 19.32$ kJ mol^{-1}

ENTHALPY OF NEUTRALIZATION

When a solution of hydrochloric acid (acid) is added to a solution of sodium hydroxide (base) dissolved in water, heat is released. This is called **enthalpy of neutralization** and the reaction may be represented as :

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l) + \text{Heat}$

In the case of strong acids and bases, the net reaction in the neutralisation is the combination of hydrogen ions (H^+) and hydroxyl ions (OH^-) to form water as :

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

$\Delta_n H^\circ = -57.1$ kJ mol^{-1}

Thus, **enthalpy of neutralization** may be defined as

enthalpy change when one mole of H^+ (*aq*) from an acid are completely neutralized by a base or one mole of OH^- (*aq*) from a base are completely neutralized by an acid.

Some examples of enthalpy of neutralisation are :

(*i*) Neutralisation of HCl with NaOH

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

$\Delta_n H^\circ = -57.1$ kJ

(*ii*) Neutralisation of CH_3COOH with NaOH

$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa + H_2O(l)$;

$\Delta_n H^\circ = -55.9$ kJ

It is very interesting to note that **enthalpy of neutralisation of all strong acids by strong bases is always equal to –57.1 kJ irrespective of the nature of acid or the base.** This can be explained on the basis of Arrhenius theory of electrolytic dissociation. According to this theory, strong acids and strong bases are completely ionised in aqueous solutions. The neutralisation reactions between strong acids and strong bases in aqueous solutions involve simply the combination of one mole H^+ ions (from an acid) and 1 mole of OH^- ions (from a base) to form unionised water molecules.

For example, let us consider the reaction between hydrochloric acid and sodium hydroxide solution. The neutralisation can be represented as :

$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$;

$\Delta H = -57.1$ kJ

Cancelling common ions :

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$;

$\Delta H = -57.1$ kJ

Similarly, the reaction between nitric acid and sodium hydroxide may be represented as :

$H^+(aq) + NO_3^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow Na^+(aq) + NO_3^-(aq) + H_2O(l)$;

$\Delta H = -57.1$ kJ

Cancelling common ions :

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$;

$\Delta H = -57.1$ kJ

Neutralisation of weak acids and weak bases. The enthalpy of neutralisation of a weak acids or weak bases do not undergo complete ionisation in aqueous solutions. Therefore, the aqueous solutions containing 1 mole of different monobasic weak acids do not contain 1 mole of H^+ ions. Similarly, the aqueous

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solutions containing 1 mole of different monoacidic weak bases do not contain 1 mole of OH^- ions. The weak acids or weak bases therefore, have to be dissociated to give 1 mole of H^+ or OH^- ions. Thus, neutralisation of weak acid and strong base (or a weak base and strong acid) not only involves the combination of H^+ ions and OH^- ions but also the dissociation of a weak acid (or a weak base). The dissociation process is accompanied by the absorption of energy and is called **enthalpy of dissociation.** Therefore, the overall liberated energy is less than 57.1 kJ (*i.e.*, 57.1 kJ – heat of dissociation of acid or base). Let us consider the neutralisation of acetic acid with sodium hydroxide.

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

Strong base (complete ionisation)

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

Weak acid $\Delta H = +1.2$ kJ

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l); \quad \Delta H = -57.1 \text{ kJ}$$

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq) + H_2O(l); \quad \Delta_n H = -55.9 \text{ kJ}$$

Thus, enthalpy of neutralisation of acetic acid and sodium hydroxide is –55.9 kJ, because 1.2 kJ heat energy is used up in dissociating acetic acid. Similarly, heat of neutralisation of ammonium hydoxide and hydrochloric acid is –51.5 kJ as 5.6 kJ is the heat of dissociation of NH_4OH.

KEY NOTE

It is **important to note** that the term gram equivalent is used in the definition of heat of neutralization. This is because neutralisation involves 1 mole of H^+ ions and 1 mol of OH^- ions to form 1 mol of water and 57.1 kJ of heat is liberated.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \quad \Delta H = -57.1 \text{ kJ}$$

Now, one gram equivalent of various acids on complete dissociation liberates one mole of H^+ ions. But one mole of the acid may produce more than one mole of H^+ ions in solution depending upon its basicity. For example, 1 mol of H_2SO_4 gives 2 mol of H^+ ions and 1 mol of H_3PO_4 gives 3 mol of H^+ ions on complete dissociation. But 1 gram equivalent of both (H_2SO_4 or H_3PO_4) produce only 1 mol of H^+ ions.

1 mol of $H_2SO_4 \equiv 2$ mol of H^+ ions,

1 gm equiv. of $H_2SO_4 \equiv 1$ mol of H^+ ions

Thus, it is more appropriate to use the term gram equivalent in the definition of enthalpy of neutralisation.

❑ **Example 41.**

Whenever an acid is neutralised by a base, the net reaction is :

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) + 57.1 \text{ kJ}$$

Calculate the heat evolved for the following experiments :

(i) 0.25 mol of HCl solution is neutralised by 0.25 mol of NaOH solution.

(ii) 0.60 mol of HNO_3 solution is mixed with 0.30 mol of KOH solution.

(iii) 100 cm^3 of 0.2 M HCl is mixed with 200 cm^3 of 0.3 M NaOH.

(iv) 400 cm^3 of 0.2 M H_2SO_4 is mixed with 600 cm^3 of 0.1 M NaOH solution.

Solution: According to the reaction,

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) + 57.1 \text{ kJ}$$

When 1 mole of H^+ ions and 1 mol of OH^- ions are neutralised to form 1 mol of water, 57.1 kJ of energy is released.

(*i*) Heat evolved for the neutralisation of 0.25 mol of NaOH solution by 0.25 mol of HCl solution.

In this case, HCl is a strong acid and NaOH is a strong base. Therefore, these ionise completely in solution to give H^+ and OH^- respectively as :

0.25 mol of HCl ≡ 0.25 mol of H^+ ions

0.25 mol of NaOH ≡ 0.25 mol of OH^- ions

On mixing or neutralisation, the net reaction is :

H^+ (0.25 mol) + OH^- (0.25 mol) = H_2O (0.25 mol)

Now, heat evolved when 1 mol of H^+ ions combines with 1 mol of OH^- ions to form 1 mol of H_2O = 57.1 kJ

∴ Heat evolved for the formation of 0.25 mol of H_2O

$= 57.1 \times 0.25$

$= \mathbf{14.3 \text{ kJ}}$

(*ii*) Heat evolved on mixing 0.60 mol of HNO_3 with 0.30 mol of KOH solution.

Since HNO_3 and KOH are strong acids and bases.

0.60 mol of HNO_3 ≡ 0.60 mol of H^+ ions

0.30 mol of KOH ≡ 0.30 mol of OH^- ions

In this case, out of 0.60 mol of H^+ ions (from HNO_3) only 0.30 mol will be neutralised (equal to OH^- ions present) by the base. 0.3 mol of H^+ ions of HNO_3 will remain unreacted. The net reaction is :

H^+ (0.30 mol) + OH^- (0.30 mol) ⟶ H_2O (0.30 mol)

Now, heat evolved during the formation of 1 mol of H_2O

$= 57.1$ kJ

∴ Heat evolved in the formation of 0.3 mol of H_2O

$= 57.1 \times 0.3 = \mathbf{17.13 \text{ kJ}}$

(*iii*) Heat evolved on mixing 100 cm^3 of 0.2 M HCl and 200 cm^3 of 0.3 M NaOH.

HCl is a strong acid and ionises completely.

Now, $HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$

1000 cm^3 of 0.2 M HCl ≡ 0.2 mol of H^+ ions

100 cm^3 of 0.2 M HCl will give H^+ ions $= \frac{0.2}{1000} \times 100$

$= 0.02$ mol

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NaOH is also a strong base and therefore, ionises completely as :

$$NaOH\ (aq) \longrightarrow Na^+\ (aq) + OH^-\ (aq)$$

1000 cm^3 of 0.3 M NaOH ≡ 0.30 mol of OH^- ions

200 cm^3 of 0.3.M NaOH will give OH^- ions

$$= \frac{0.3 \times 200}{1000} = 0.06 \text{ mol}$$

0.02 mol of H^+ ions would combine with 0.02 mol of OH^- ions to form 0.02 mol of H_2O and 0.04 (0.06 – 0.02) mol of OH^- ions remain unreacted. The net reaction is :

$$H^+\ (0.02 \text{ mol}) + OH^-\ (0.02 \text{ mol}) \longrightarrow H_2O\ (0.02 \text{ mol})$$

Heat evolved for the formation of 1 mol of H_2O = 57.1 kJ

∴ Heat evolved for the formation of 0.02 mol of H_2O = 57.1 × 0.02 = **1.14 kJ**

(*iv*) Heat evolved on mixing 400 cm^3 of 0.2 M H_2SO_4 with 600 cm^3 of 0.1 M NaOH.

H_2SO_4 is a dibasic strong acid. One mol of H_2SO_4 gives 2 mol of H^+ ions

$$H_2SO_4\ (aq) \rightleftharpoons 2H^+\ (aq) + SO_4^{2-}\ (aq)$$

1000 cm^3 of 0.2 M H_2SO_4 ≡ 0.2 × 2 mol of H^+ ions

400 cm^3 of 0.2 M H_2SO_4 will give H^+ ions

$$= \frac{0.2 \times 2}{1000} \times 400 = 0.16 \text{mol.}$$

Similarly,

1000 cm^3 of 0.1 M NaOH ≡ 0.1 of OH^- ions

∴ 600 cm^3 of 0.1 M NaOH will give OH^- ions

$$= \frac{0.1 \times 600}{1000} = 0.06 \text{ mol}$$

Now, out of 0.16 mol of H^+ ions, only 0.06 mol will be neutralised by OH^- ions of the base and 0.10 mol (0.16 – 0.06) of H^+ ions are left unreacted. The net reaction is :

$$H^+\ (0.06) \text{ mol} + OH^-\ (0.06 \text{ mol}) \longrightarrow H_2O\ (0.06 \text{ mol})$$

Heat evolved for the formation of 1 mol of H_2O = 57.1 kJ

∴ Heat evolved for the formation of 0.06 mol of H_2O = 57.1 × 0.06 = **3.43 kJ**

ENTHALPY OF PHASE TRANSITIONS

It is a common experience that energy is required to convert a solid into a liquid (melting) or liquid into a gas (evaporation). This is because of the fact that the intermolecular forces in the three states of matter (solid, liquid or gas) are different. These processes are called **phase changes** or **phase transitions.** The enthalpy changes or heat changes accompanying these phase changes are described below :

1. Enthalpy of Fusion

The enthalpy change when 1 mole of a solid substance is converted into its liquid state at its melting point *is called* **enthalpy of fusion.** It is also called **molar enthalpy of fusion.** In other words, **it is the enthalpy change that accompanies melting of one mole of solid.**

When the process of melting is carried out at constant temperature and under standard pressure (1 bar) it is called **standard enthalpy of fusion, $\Delta_{fus}H°$.**

For example, when one mole of ice melts at 0°C (or 273 K), the heat absorbed is 6.0 kJ. This corresponds to the process :

$$\underset{\text{(Ice)}}{H_2O(s)} \longrightarrow \underset{\text{(Water)}}{H_2O(l)} \quad \text{or} \quad \Delta_{fus}H° = 6.0 \text{ kJ mol}^{-1}$$

Here $\Delta_{fus}H^o$ is standard enthalpy of fusion. If water freezes, then process is reversed and an equal amount of heat is evolved. Thus,

$$\Delta_{freeze}H^o = -\Delta_{fus}H^o$$

$$\therefore \quad \Delta_{freeze}H^o = -6.0 \text{ kJ mol}^{-1}$$

Similarly, the enthalpy of fusion of ethyl alcohol at 156 K is + 4.8 kJ mol^{-1}.

$$C_2H_5OH(s) \longrightarrow C_2H_5OH\ (l) \text{ at } 156 \text{ K}$$

$$\Delta_{fus}H° = +4.8 \text{ kJ mol}^{-1}$$

Enthalpy of fusion may also be expressed as

$$\Delta_{fus}H^o = H^o_{liquid} - H^o_{solid}$$

Melting of solid is endothermic so enthalpy of fusion is always **positive.**

It may be noted that enthalpies of fusion of substances give an idea of the nature of solid and the magnitude of forces acting between the particles constituting the solids (atoms, molecules or ions). The solids such as O_2, H_2S, CCl_4, etc. which are molecular solids (consisting of molecules) have low enthalpies of fusion because the forces of attraction between their molecules are weak forces. For example,

$$\Delta H_{fus}H^o\ [O_2] \text{ at } 55 \text{ K} = +0.45 \text{ kJ mol}^{-1}$$

$$\Delta H_{fus}H^o\ [H_2S] \text{ at } 188 \text{ K} = +2.0 \text{ kJ mol}^{-1}$$

$$\Delta H_{fus}H^o\ [CCl_4] \text{ at } 250 \text{ K} = +2.5 \text{ kJ mol}^{-1}$$

On the other hand, ionic solids such of NaCl, $MgCl_2$, etc. have high enthalpies of fusion because they have strong electrostatic forces of attraction between the ions constituting them. For example,

$$\Delta H_{fus}H^o\ [NaCl] \text{ at } 1074 \text{ K} = +29.0 \text{ kJ mol}^{-1}$$

$$\Delta H_{fus}H^o\ [MgCl_2] \text{ at } 1260 \text{ K} = +43.0 \text{ kJ mol}^{-1}$$

2. Enthalpy of Vaporisation

The enthalpy change when 1 mole of a liquid is converted into gaseous state at its boiling point, *is called* **enthalpy of vaporization** or **molar enthalpy of vaporisation.** In other words, **it is the enthalpy change accompanying the vaporization of one mole of liquid.**

When the process of vaporization is carried out at constant temperature and under standard pressure (1 bar), it is called standard enthalpy of vaporization, $\Delta_{vap}H^o$.

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For example, the heat change accompanying the vaporisation of 1 mol of water (liquid) into gas (steam) at 100°C (373 K) is 40.6 kJ and is represented as

$$H_2O(l) \longrightarrow H_2O(g) \text{ at } 373 \text{ K}$$
$$\Delta_{vap}H^\circ = 40.79 \text{ kJ mol}^{-1}$$

Enthalpies of vaporisation of ethyl alcohol at 334 K and of benzene at 349 K are + 30.5 kJ mol^{-1} and 30.8 kJ mol^{-1} respectively. Enthalpies of vaporisation also give an idea about the magnitude of forces of attraction between the particles constituting the liquids. *Greater the value, more will be the magnitude of the attractive forces.* For example, the strong hydrogen bonds between water molecules hold them tightly in liquid phase. For an organic liquid such as acetone, the intermolecular dipole–dipole interactions are significantly weaker. Thus, it requires less heat to vaporise 1 mole of acetone than it does to vaporise 1 mole of water.

3. Enthalpy of Sublimation (or Heat of Sublimation)

The enthalpy change when one mole of a solid is directly converted into its gaseous state at a temperature below its melting point *is called* **enthalpy of sublimation** or **molar enthalpy of sublimation.**

We know that sublimation is a process in which a solid changes into gaseous state below its melting point. For example, when one mole of solid iodine sublimes, the heat change is 62.4 kJ and is represented as :

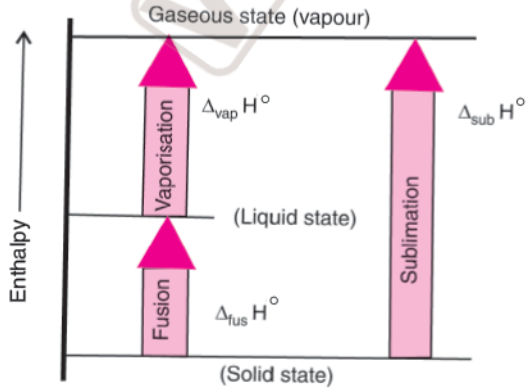
$$I_2(s) \longrightarrow I_2(g) \qquad \Delta_{sub}H^\circ = +62.4 \text{ kJ}$$

Similarly, naphthalene sublimes slowly and for this $\Delta_{sub}H^\circ$ is 73.0 kJ mol^{-1} and dry ice (solid CO_2) sublimes at 195 K and has $\Delta_{sub}H^\circ$ = 25.2 kJ mol^{-1}.

The enthalpy of sublimation is related to enthalpy of fusion and enthalpy of vaporisation as :

$$\Delta_{sub}H^\circ = \Delta_{fus}H^\circ + \Delta_{vap}H^\circ$$

This is shown below :



For example, at 298 K, enthalpy of fusion (Δ_fH°) of sodium metal is 2.6 kJ mol^{-1} and enthalpy of vaporisation of liquid sodium ($\Delta_{vap}H^\circ$) is 98.0 kJ mol^{-1}. Thus, enthalpy of sublimation of solid sodium at 298 K is

$$\Delta_{sub}H^\circ = \Delta_{fus}H^\circ + \Delta_{vap}H^\circ$$
$$= 2.6 + 98.0 = 100.6 \text{ kJ mol}^{-1}.$$

Enthalpy of fusion and vaporisation of some compounds are given in Table 6.

Table 6. Enthalpy of fusion and vaporisation of different substances.

Substance	m.p. (K)	$\Delta_{fus}H^\circ$ (kJ mol^{-1})	b.p. (K)	$\Delta_{vap}H^\circ$ (kJ mol^{-1})
Helium (He)	3	0.021	4	0.092
Hydrogen (H_2)	14	+0.12020		+0.904
Oxygen (O_2)	55	+0.45	90	+6.7
Nitrogen (N_2)	63	0.72	77.3	5.59
Ammonia (NH_3)	195.4	5.65	239.7	23.35
Hydrogen chloride (HCl)	159	+1.99	188	16.15
Carbon tetrachloride (CCl_4)	250	+2.5	350	+30.0
Carbon monoxide (CO)	68.0	6.84	82.0	6.04
Acetone (CH_3COCH_3)	177.8	5.72	329.4	29.1
Bromine (Br_2)	266	+5.3	334	+30.5
Ethyl alcohol (C_2H_5OH)	156	+4.8	351	+34.7
Benzene (C_6H_6)	278.5	+9.8353		+30.79
Water (H_2O)	273	+6.0	373	+40.6
Sodium (Na)	371	+2.6	1115	+98.0
Sodium chloride (NaCl)	1081	+28.81665		+170.0
Magnesium chloride ($MgCl_2$)	1260	+43.0	1691	137.0

SOLVED EXAMPLES

Example 42.

When 1 g of liquid naphthalene ($C_{10}H_8$) solidifies, 149 J of heat is evolved. Calculate the heat of fusion of naphthalene.

Solution:

Molecular mass of naphthalene,

$$C_{10}H_8 = 10 \times 12 + 8 \times 1 = 128$$

For the solidification reaction

$$C_{10}H_8(l) \longrightarrow C_{10}H_8(s)$$

Heat evolved when 1 g of naphthalene solidifies = 149 J

Heat evolved when 128 g of naphthalene solidify = 149 × 128 = 19072 J

i.e., $C_{10}H_8(l) \longrightarrow C_{10}H_8(s)$ $\quad \Delta_{fus}H^\circ = -19072$ J

For the fusion reaction,

$$C_{10}H_8(s) \longrightarrow C_{10}H_8(l)$$

This reaction is the reverse of the above solidification reaction so that

$$\Delta_{fus}H^\circ = -\Delta_{solid}H^\circ$$

Thus, $\Delta_{fus}H^\circ$ = **19072 J** or = **19.072 kJ**

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❑ **Example 43.**

Calculate the enthalpy change when 2.38 g of carbon monoxide (CO) vaporize at its normal boiling point. Enthalpy of vaporization of CO is 6.04 kJ mol^{-1}. **N.C.E.R.T.**

Solution: Enthalpy of vaporisation of CO
= 6.04 kJ mol^{-1}.

Molar mass of CO = 28 g mol^{-1}

Enthalpy change for vaporisation of 28 g of CO at boiling point = 6.04 kJ mol^{-1}

Enthalpy change when 2.38 g of CO vaporize at

$$\text{boiling point} = \frac{6.04}{28} \times 2.38$$

$$= 0.5134 \text{ kJ} = \mathbf{513.4\ J}$$

❑ **Example 44.**

A boy after swimming comes out from a pool covered with a film of water weighing 18 g. How much heat must be supplied to evaporate this water at 298K ? Calculate the internal energy of vaporisation at 100°C. ΔH°_{vap} for water at 373 K = 40.66 kJ mol^{-1} **N.C.E.R.T.**

Solution: $\Delta_{vap}H^\circ = 40.66$ kJ mol^{-1}

$$H_2O\ (l) \xrightarrow{\text{Vaporise}} H_2O\ (g)$$

Molar mass of water = 18 g mol^{-1}

Mass of water = 18 g

$$\text{Moles of water} = \frac{18}{18} = 1 \text{ mol}$$

Heat needed for vaporisation = $n\Delta_{vap}H^\circ$
= 1 mol × 40.66 kJ mol^{-1}
= 40.66 kJ

Now $\Delta_{vap}U = \Delta_{vap}H^\circ - p\Delta V$
$= \Delta_{vap}H^\circ - \Delta n_g RT$
$\Delta n_g = 1 - 0 = 1$ mol

Assuming steam behaving as an ideal gas

$\Delta_{vap}U = \Delta_{vap}H^\circ - \Delta n_g RT$
$= 40.66 - (1)\ 8.314 \times 10^{-3} \times 373$
$= 40.66 - 3.10$
= 37.56 kJ mol^{-1}

❑ **Example 45.**

18.0 g of water completely vapourises at 100°C and 1 bar pressure and the enthalpy change for the process is 40.79 kJ mol^{-1}.

(i) What will be the enthalpy change for vapourising 2 moles of water under the same conditions ?

(ii) What is the standard enthalpy of vapourisation for water ? *(NCERT Exemplar Problem)*

Solution:

$$\text{Moles of water} = \frac{18.0}{18} = 1.0 \text{ mol}$$

Enthalpy change for vapourisation of 1 mol of water = 40.79 kJ mol^{-1}

(*i*) Enthalpy change for vapourisation of 2 mol of water = 40.79 × 2 = 81.58 kJ mol^{-1}

(*ii*) Standard enthalpy of vapourisation = Enthalpy change for vapourisation of 1 mol of water = 40.79 kJ mol^{-1}.

ENTHALPY OF ATOMIZATION AND BOND ENTHALPY.

Enthalpy of Atomization

Consider the following example of atomization of dihydrogen into hydrogen atoms.

$H_2(g) \longrightarrow H(g) + H(g) \qquad \Delta_aH^\circ = 435.0$ kJ mol^{-1}

Since in these reactions H atoms are formed by breaking of H—H bonds in dihydrogen, so this is known as **enthalpy of atomization** and is represented as Δ_aH°. **Enthalpy of atomization** may be defined as

the enthalpy change in breaking one mole of bonds completely into atoms in the gaseous state.

In case of diatomic molecules, like dihydrogen, the enthalpy of atomization is also called **bond dissociation enthalpy.** The other example of enthalpy of atomization can be

$CH_4(g) \longrightarrow C(g) + 4H(g);\ \Delta_aH^\circ = 1665$ kJ mol^{-1}

It may be noted that in this reaction, the products are only **atoms** of carbon and hydrogen in the gaseous state.

Consider the following reaction :

$Na(s) \longrightarrow Na(g); \qquad \Delta_aH^\circ = 108.4$ kJ mol^{-1}

In this case, the enthalpy of atomization is same as the enthalpy of sublimation.

Similarly, the bond dissociation enthalpies or atomization of Cl—Cl in Cl_2 is 242.5 kJ mol^{-1}, I—I in I_2 is 15.1 kJ mol^{-1}, H—I in HI is 299 kJ mol^{-1}, etc.

Bond Dissociation Enthalpy and Bond Enthalpy

Chemical reactions involve the breaking and making of chemical bonds. When a bond is formed between the atoms, energy is released. Obviously, the same amount of energy will be needed to break the bond enthalpy.

It is possible to relate heat of reaction to changes in energy associated with breaking and making of chemical bonds. Generally, two different terms are used in thermodynamics for expressing enthalpy changes associated with chemical bonds. These are :

(*i*) Bond dissociation enthalpy and

(*ii*) Mean or average bond enthalpy

These enthalpy changes depend upon the nature of the bond and also nature of the molecule in which the bond is present. These are measure of strengths of bonds.

Bond Dissociation Enthalpy

The amount of energy required to break one mole of bonds of a particular type between the atoms in the gaseous state is called ***bond dissociation enthalpy.***

It is generally expressed in terms of kJ/mol. For example, 435 kJ of energy is required to break or dissociate the H—H bonds in one mole of H_2 molecules, therefore, the bond dissociation enthalpy of H—H bond is 435 kJ mol^{-1} at 298 K.

$H_2(g) \longrightarrow 2H(g) : \Delta_{H-H}H^\circ = 435.0$ kJ mol^{-1}

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It may be noted that it is the same as the enthalpy of atomization of dihydrogen. It is also true for all diatomic molecules. For example,

$Cl_2(g) \longrightarrow 2Cl(g) : \Delta_{Cl-Cl}H^\circ = 242 \text{ kJ mol}^{-1}$

$O_2(g) \longrightarrow 2O(g) : \Delta_{O-O}H^\circ = 428 \text{ kJ mol}^{-1}$

However, in case of polyatomic molecules, which contain more than one bond of the same kind, the bond dissociation enthalpy is different for different bonds within the same molecule. Therefore, **mean** or **average value** of the bond dissociation enthalpies of a given bond is taken.

The average of the bond dissociation enthalpies required to dissociate a particular type of bond in a substance is called **bond enthalpy.**

For example, in water, there are two O—H bonds. The bond dissociation enthalpies of two O—H bonds in water are:

$H_2O(g) \longrightarrow H(g) + OH(g); \Delta_rH^\circ = 497.8 \text{ kJ}$

$OH(g) \longrightarrow H(g) + O(g); \Delta_rH^\circ = 428.5 \text{ kJ}$

The bond enthalpy is the average of these two bond dissociation enthalpies, *i.e.*,

$$\text{Bond enthalpy of O—H bond} = \frac{497.8 + 428.5}{2}$$

$$= 463.15 \text{ kJ mol}^{-1}$$

Similarly, in methane, all the four C—H bonds are identical in bond length and energy. However, the energies required to break the individual C—H bonds in each successive step differ. The overall thermochemical equation for atomization reaction of methane is :

$CH_4(g) \longrightarrow C(g) + 4H(g) \Delta_rH^\circ = 1665 \text{ kJ mol}^{-1}$

The energies required to break the individual C – H bonds are :

$CH_4(g) \longrightarrow CH_3(g) + H(g) \Delta_rH^\circ = 427 \text{ kJ mol}^{-1}$

$CH_3(g) \longrightarrow CH_2(g) + H(g) \Delta_rH^\circ = 439 \text{ kJ mol}^{-1}$

$CH_2(g) \longrightarrow CH(g) + H(g) \Delta_rH^\circ = 452 \text{ kJ mol}^{-1}$

$CH(g) \longrightarrow C(g) + H(g) \Delta_rH^\circ = 347 \text{ kJ mol}^{-1}$

Adding these equations,

$CH_4(g) \longrightarrow C(g) + 4H(g)$

$$\Delta_aH^\circ = 427 + 439 + 452 + 347$$

$$= 1665 \text{ kJ mol}^{-1}$$

The average bond enthalpy of C – H bond is

$$\text{B.E.} = \frac{1}{4}(\Delta_aH^\circ) = \frac{1665 \text{ kJ mol}^{-1}}{4}$$

$$= 416.25 \text{ kJ mol}^{-1}.$$

Thus, we observe that average bond enthalpy of C-H bond in methane is 416.25 kJ mol^{-1}. It has been found that average C–H bond enthalpies differ slightly from compound to compound as in CH_3Cl, CH_2Cl_2, CH_3NO_2 etc. but the difference is not large. The bond enthalpies can be calculated by using Hess's law. Bond enthalpy values of some single and multiple bonds are given in Table 7 and 8.

Table. 7 Some average single bond enthaplies in kJ mol^{-1}

	H	C	N	O	F	Si	P	S	Cl	Br	I
H	436	414	389	464	569	293	318	339	431	368	297
C		347	293	351	439	289	264	259	330	276	238
N			159	201	272	–	209	–	201	(243)	–
O				138	184	368	351	–	205	–	201
F					159	540	490	327	255	(197)	–
Si						176	213	226	360	289	213
P							213	230	331	272	213
S								213	251	213	–
Cl									243	218	209
Br										192	180
I											151

Table 8. Some average multiple bond enthalpies (in kJ mol^{-1})

Bond	Bond Enthalpy	Bond	Bond enthalpy	Bond	Bond Enthalpy
N = N	418	C = C	611	O = O	498
N ≡ N	946	C ≡ C	837		
C = N	615	C = O	741		
C ≡ N	891	C ≡ O	1070		

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An important use of the bond enthalpy is that it helps to calculate the enthalpy of formation of atoms. For example, consider the reaction :

$H_2(g) \longrightarrow 2H(g) \qquad \Delta H^\circ = 435.0 \text{ kJ mol}^{-1}$

It is clear that the bond dissociation enthalpy (ΔH°) is twice the formation of hydrogen atom in the gaseous state so that

$$\frac{1}{2}H_2(g) \longrightarrow H(g)$$

$$\Delta H^\circ = \frac{435}{2} = 217.5 \text{ kJ mol}^{-1}$$

Thus, $\Delta_f H^\circ$ (H, g) = –217.5 kJ mol^{-1}

KEY NOTE

Strictly speaking, the amount of energy required to dissociate one mole of bond should be bond dissociation energy or bond energy, ΔU°. However, we commonly use bond enthalpy or bond dissociation enthalpy. The value $\Delta_a H^\circ = 435.0$ kJ mol^{-1} is the bond enthalpy of H – H bond. The corresponding $\Delta_a U^\circ$ is 430.8 kJ mol^{-1}. Thus, there is only a small difference between the two quantities and therefore, it may be ignored. We very often use these terms interchangeably.

It may be noted that for diatomic molecules bond dissociation enthalpy and bond enthalpy are same.

Use of bond enthalpies to calculate enthalpy change of reactions. The bond enthalpy data can also be used to calculate the enthalpy change of many reactions. The chemical reaction involves the cleavage of old bonds in reactants and formation of new bonds in products. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in the reactant molecules minus the amount of energy required to break all the bonds in the product molecules. Enthalpy change of the reaction may be given as :

Enthalpy of reaction

$$= \begin{bmatrix}\text{Sum of bond enthalpies}\\ \text{of reactants}\end{bmatrix} - \begin{bmatrix}\text{Sum of bond}\\ \text{enthalpies of products}\end{bmatrix}$$

$$\Delta_r H^\circ = \sum \begin{matrix}\text{Bond enthalpies}\\ \text{of reactants}\end{matrix} - \sum \begin{matrix}\text{Bond enthalpies}\\ \text{of products}\end{matrix}$$

For example, consider the reaction,

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

In this reaction, it is clear that one H—H bond and one Br—Br bond break while two H—Br bonds are formed,

$\therefore \quad \Delta_r H^\circ$ = B.E. (H—H) + B.E.(Br—Br) – 2 B.E.(H—Br)

The bond enthalpies of different bonds have been found to be

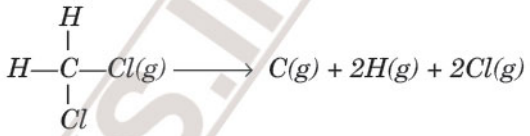
H—H bond = 435 kJ, Br—Br bond = 192 kJ, H—Br bond = 368 kJ

$\therefore \quad \Delta_r H^\circ = 435 + 192 - 2 \times 368 =$ **–109 kJ.**

SOLVED EXAMPLES

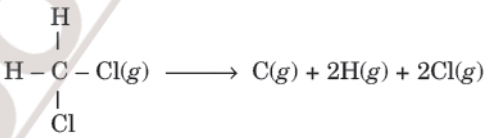
Example 46.

Calculate $\Delta_r H^\circ$ for the reaction :



Average bond enthalpies of C – H and C – Cl bonds are 414 kJ mol^{-1} and 330 kJ mol^{-1} respectively.

Solution:



In this reaction, 2C – H and 2C – Cl bonds are broken and no new bonds are formed. Therefore,

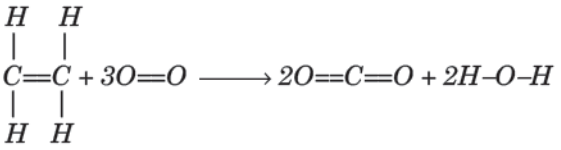
$\Delta_r H^\circ$ = [2 × (Bond enthalpy of C – H bond)] + 2 × [(Bond enthalpy of C – Cl bond)]

= 2 × 414 kJ + 2 × 330 kJ

= **1488 kJ.**

Example 47.

Calculate $\Delta_r H^\circ$ for the reaction,



The average bond enthalpies of various bonds are :

Bond	*C–H*	*O=O*	*C=O*	*O–H*	*C=C*
Bond enthalpy (kJ mol^{-1})	*414*	*499*	*724*	*460*	*619*

Solution: In this reaction, four C–H bonds, one C = C bond and three O = O bonds are broken and four C=O bonds and four O–H bonds are formed. Thus,

ΔH° =[4 × (Bond enthalpy of C–H) + (Bond enthalpy of C = C) + 3 (Bond enthalpy of O = O)] – [4 × (Bond enthalpy of C = O) + 4 (Bond enthalpy of O—H)]

ΔH = (4 × 414 + 619 + 3 × 499) – (4 × 724 + 4 × 460)

= **–964 kJ mol^{-1}**

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Example 48.

Calculate C–C bond enthalpy from the following data :

$2C\ (graphite) + 3H_2(g);\ \longrightarrow\ C_2H_6(g)$
$\Delta_r H^\circ = -84.67\ kJ$

$C\ (graphite);\ \longrightarrow\ C(g)$
$\Delta_r H^\circ = 716.7\ kJ$

$H_2(g);\ \longrightarrow\ 2H(g)$
$\Delta_r H^\circ = 435.9\ kJ$

Assume 416 kJ as the C–H bond enthalpy.

Solution: The given equations are :

(*i*) $2C\ (graphite) + 3H_2(g) \longrightarrow C_2H_6(g);\ \Delta_r H^\circ = -84.67\ kJ$

(*ii*) $C\ (graphite) \longrightarrow C(g);\ \Delta_r H^\circ = 716.7\ kJ$

(*iii*) $H_2(g) \longrightarrow 2H(g);\ \Delta_r H^\circ = 435.9\ kJ$

Multiply eq. (*ii*) by 2 and (*iii*) by 3 and add

(*ii*) × 2; $2\ C(graphite) \longrightarrow 2C(g);\ \Delta_r H^\circ = 1433.4\ kJ$

(*iii*) × 3; $3H_2(g) \longrightarrow 6H(g);\ \Delta_r H^\circ = 1307.7\ kJ$

Adding (*iv*) $2C\ (graphite) + 3H_2(g) \longrightarrow 2C(g) + 6H(g);\ \Delta_r H^\circ = 2741.1\ kJ$

Subtract eq. (*i*) from (*iv*)

(*i*) $2C\ (graphite) + 3H_2(g) \longrightarrow C_2H_6(g);\ \Delta_r H^\circ = -84.67\ kJ$

Subtracting $C_2H_6(g) \longrightarrow 2C(g) + 6H(g);\ \Delta_r H^\circ = 2825.77\ kJ$

C_2H_6 has six C – H bonds and one C – C bond so that

$\Delta_r H^\circ$ = [Bond enthalpy of C – C bond] + 6 [Bond enthalpy C – H bond]

or Bond enthalpy of C – C bond = $\Delta_r H^\circ$ – 6 [Bond enthalpy of C – H bond]

$\therefore$ Bond enthalpy of C—C bond
= 2825.77 – 6(416)
= 2825.77 – 2496 = **329.77 kJ mol^{-1}.**

Example 49.

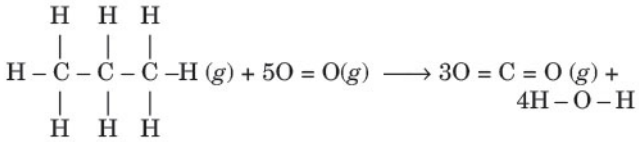
Propane has the structure $H_3C - CH_2 - CH_3$. Calculate the enthalpy change, $\Delta_r H^\circ$ for the reaction :

$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$

The average bond enthalpies of various bonds are

	C – C	C — H	O = O	C = O	O — H
(kJ mol^{-1})	347	414	498	741	464

Solution: The reaction is



In this reaction, two C – C, eight C – H and five O = O bonds are broken and six C = O bonds and eight O – H bonds are formed. Thus,

$\Delta_r H^\circ$ = Σ Bond enthalpies of reactants – Σ Bond enthalpies of products

= 2 (Bond enthalpy of C – C) + 8 (Bond enthalpy of C – H) + 5 (Bond enthalpy of O = O) – 6 (Bond enthalpy of C = O) – 8 (Bond enthalpy of O – H)

= 2(347) + 8(414) + 5(498) – 6(741) – 8(464)

= 6496 – 8158

= **– 1662 kJ mol^{-1}.**

Example 50.

Calculate the enthalpy change for the process :

$CCl_4(g) \longrightarrow C(g) + 4\ Cl\ (g)$

and calculate bond enthalpy of C–Cl bond in $CCl_4(g)$

$\Delta_{vap}H^\circ\ (CCl_4) = 30.5\ kJ\ mol^{-1}$
$\Delta_f H^\circ\ (CCl_4) = -135.5\ kJ\ mol^{-1}$
$\Delta_a H^\circ\ (C) = 715.0\ kJ\ mol^{-1}$
$\Delta_a H^\circ\ (Cl_2) = 242\ kJ\ mol^{-1}$

N.C.E.R.T.

Solution: The enthalpy change for the reaction :

$CCl_4(g) \longrightarrow C(g) + 4\ Cl\ (g)$
$\Delta H^\circ = \Delta_a H^\circ(C) + 4\ \Delta_a H^\circ\ (Cl) - \Delta_f H^\circ\ (CCl_4)\ (g)$
$\Delta_a H^\circ\ (C) = 715.\ 0\ kJ\ mol^{-1}$
$\Delta_a H^\circ\ (Cl_2) = 242\ kJ\ mol^{-1}$
Let us first calculate $\Delta_f H^\circ\ [CCl_4\ (g)]$

$C(s) + 2Cl_2(g) \longrightarrow CCl_4\ (l) \Delta H^\circ = -135.5\ kJmol^{-1}$

$CCl_4\ (l) \longrightarrow CCl_4\ (g)\ \Delta H^\circ = 30.5\ kJ\ mol^{-1}$

Adding $C(s) + 2Cl_2\ (g) \longrightarrow CCl_4(g)$
$\Delta H^\circ = -105.0\ kJ\ mol^{-1}$

$\therefore\ \Delta H^\circ = 715.0 + 2 \times 242 - (-105.0) = 1304.0\ kJ\ mol^{-1}$

This enthalpy change corresponds to breaking of four C–Cl bonds

$\therefore$ Bond enthalpy of C-Cl bond $= \dfrac{1304.0}{4}$
= **326** kJ mol^{-1}

Example 51.

Calculate the bond enthalpy of C—H bond given that the enthalpy of formation of CH_4, enthalpy of sublimation of carbon and bond dissociation enthalpy of H_2 are –74.8, + 719.6 and 435.4 kJ mol^{-1} respectively.

Solution: The given equations are :

(*i*) $C(s) + 2H_2(g) \longrightarrow CH_4(g)$ $\Delta_r H^\circ = -74.8\ kJ$
(*ii*) $C(s) \longrightarrow C(g)$ $\Delta_r H^\circ = 719.6\ kJ$
(*iii*) $H_2(g) \longrightarrow 2H(g)$ $\Delta_r H^\circ = +435.4\ kJ$

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The required equation is

$$CH_4(g) \longrightarrow C(g) + 4\,H\,(g)$$

Multiply eq. (*iii*) by 2 and add to eq (*ii*)

(*iii*) × 2 $2H_2(g) \longrightarrow 4\,H(g)$ $\Delta_r H° = 870.8$ kJ

(*ii*) $C(s) \longrightarrow C(g)$ $\Delta_r H° = 719.6$ kJ

Adding

(*iv*) $C(s) + 2H_2(g) \longrightarrow C(g) + 4H(g)$ $\Delta_r H° = 1590.4$ kJ

Subtract eq. (*i*) from eq. (*iv*)

$C(s) + 2H_2(g) \longrightarrow CH_4(g)$ $\Delta_r H° = -74.8$ kJ

Subtracting

$$CH_4(g) \longrightarrow C(g) + 4H(g)\ \Delta_r H° = 1665.2\ \text{kJ}$$

This gives the enthalpy of dissociation of four moles of C—H bonds. Hence, bond enthalpy of C—H bond is

$$\Delta_{C-H}H° = \frac{1665.2}{4} = 416.3\ \text{kJ mol}^{-1}.$$

Practice Problems

35. Calculate $\Delta_r H°$ for the reaction,

$$H_2\,(g) + \frac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(g)$$

Given that bond enthalpies of H-H bond, O=O bond and O - H bond are 433 kJ mol $^{-1}$, 492 kJ mol^{-1} and 464 kJ mol^{-1}

36. Calculate the enthalpy of hydrogenation :

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

Given that the bond enthalpies of H – H, C = C, C – C and C – H bonds are 433, 615, 347 and 413 kJ mol^{-1} respectively.

37. Calculate the bond enthalpy of H—Cl given that the bond enthalpies of H_2 and Cl_2 are 435.4 and 242.8 kJ mol^{-1} respectively and enthalpy of formation of HCl(g) is –92.2 kJ mol.

38. The enthalpy change for the reaction :

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$$

$$\Delta_r H^\circ = -1662\ \text{kJ mol}^{-1}$$

The bond enthalpies of different bonds (in kJ mol^{-1}) are:

C – C	C–H	C = O	O – H
347	414	741	464

Calculate bond enthalpy of O = O bond in O_2 molecules.

N.C.E.R.T.

Answers to Practice Problems

35. – 249 kJ **36.** ΔH = –125 kJ

37. 431.3 kJ mol^{-1} **38.** 498 kJ mol^{-1}

Hints & Solutions on page 78

add on Conceptual Questions 2

CONCEPTUAL QA

Q.1. Will the heat released be same or different in the following two reactions :

(*i*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ **(*ii*)** $H_2\,(g) + \frac{1}{2}\,O_2(g) \longrightarrow H_2O(g)$

Explain.

Ans. The heat released in the above two reactions will be different. It will be greater in reaction (*i*) because when water (*g*) condeneses to form water (*l*), heat is released.

Q.2. Diamond is an elementary substance, yet its standard heat of formation is not taken as zero. Why?

Ans. The common form of carbon is graphite and its standard heat of formation, $\Delta_f H°$ is taken as zero. Diamond is not common form of carbon.

$$q_P = \Delta H.$$

Q.3. What is the basis of Hess's law of heat summation ?

Ans. Enthalpy is a state fuction and it is independent of the path followed.

Q.4. Which of the following state of bromine will have standard heat of formation to be equal to zero? Liquid bromine, solid bromine, gaseous bromine molecules.

Ans. Liquid bromine because it is elementary state.

Q.5. A system is changed from an initial state by a manner so that ΔH = *q*. If the change from the initial state to the final state were made by a different path, would ΔH and *q* be the same as that for the first path ?

Ans. ΔH is same because it is a state function. *q* will most probably different for different systems because it is not state function.

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Q.6. Given that : $O(g) + e^- \longrightarrow O^-(g)$ $\Delta H = -142$ kJ mol^{-1}

$O(g) + 2e^- \longrightarrow O^{2-}(g)$ $\Delta H = +712$ kJ mol^{-1}

What will be the ΔH for the reaction :

$O^-(g) + e^- \longrightarrow O^{2-}(g)$

Ans. (*i*) $O(g) + e^- \longrightarrow O^-(g)$ $\Delta H = -142$ kJ

(*ii*) $O(g) + 2e^- \longrightarrow O^{2-}(g)$ $\Delta H = 854$ kJ.

Q.7. Can enthalpy of combustion be positive ?

Ans. No, enthalpy of combustion is always negative.

Q.8. The heat of formation of Fe_2O_3 (*s*) is –824.0 kJ. What will be the ΔH for the reaction :

$2\,Fe_2O_3(s) \longrightarrow 4Fe(s) + 3\,O_2(g)$

Ans. $\Delta_r H^\circ = 2 \times 824 = 1648$ kJ.

Q.9. The enthalpy of formation of gaseous iodine is 62.5 kJ mol^{-1}. What is the enthalpy of sublimation of iodine at 25°C ?

Ans. Enthalpy of sublimation:

$I_2(s) \longrightarrow I_2(g)$ $\Delta H_{sub.}$

So, enthalpy of sublimation of idodine (*g*) is same as the enthalpy of formation of I_2 (*g*) *i.e.* 62.5 kJ mol^{-1}

Q.10. The standard enthalpy of formation of $H_2O(l)$ and $H_2O(g)$ are –285.8 and –241.8 kJmol^{-1} respectively. What is the heat of vaporisation of water per gram at 25°C and 1 atm ?

Ans. For the vaporisation :

$$H_2O(l) \longrightarrow H_2O(g)$$

$$\Delta_r H^\circ = \Delta_f H^\circ [H_2O(g)] - \Delta_f H^\circ [H_2O(l)]$$

$$= -241.8 - (-285.8)$$

$$= 44 \text{ kJ mol}^{-1}$$

$\therefore$ Heat of vaporisation per gram $= \frac{44}{18} = 2.44$ kJ.

Q.11. Write an expression in the form of a chemical equation of the standard enthalpy of formation of CO.

Ans. $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g) : \Delta_f H^\circ = \pm$

Q.12. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ $\Delta_r H^\circ = -92.4$ kJ

What is the standard enthalpy of formation of NH_3 ?

Ans. The $\Delta_r H^\circ$ value corresponds to 2 mol of NH_3

$\therefore$ Standard enthalpy of formation of $NH_3 = \frac{-92.4}{2}$

$= -46.2$ kJ mol^{-1}

Q.13. Which of the following will have larger ΔH value and why ?

(*i*) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$

(*ii*) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$

Ans. Reaction (*ii*) will have larger value of ΔH because when $H_2O(g)$ condenses to form $H_2O(l)$, some heat is evolved (called enthalpy of condensation). Therefore, the total heat evolved becomes large.

Q.14. One kilogram of graphite is burnt in a closed vessel. The same amount of graphite is burnt in an open vessel. Will the heat evolved in two cases be same or different?

Ans. Same in both cases because Δn_g is zero.

Q.15. If enthalpy of fusion and enthalpy of vaporisation of sodium metal are 2.6 and 98.2 kJ mol^{-1} respectively, what is the enthalpy of sublimation of sodium?

Ans. $\Delta_{sub} H^\circ = \Delta_{fus} H^\circ + \Delta_{vap} H^\circ = 2.6 + 98.2 = 100.8$ kJ mol^{-1}

CONCEPTUAL QA

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Advanced Level PROBLEMS Accelerate Your Potential (for JEE Advance)

Problem 1. Calculate the enthalpy change on freezing of 1.0 mol of water at 10°C to ice at –10°C.

$\Delta_{fus}H = 6.03\ kJ\ mol^{-1}$ at 0°C

$C_p\ [H_2O(l)] = 75.3\ J\ mol^{-1}\ K^{-1}$

$C_p\ [H_2O(s)] = 36.8\ J\ mol^{-1}\ K^{-1}$

Solution The enthalpy change on freezing 1.0 mol of water from 10°C to –10°C may be expressed as :

1 mol water (10°C) $\xrightarrow{\Delta H_1}$ 1 mol water (0°C) $\xrightarrow{\Delta H_2}$

1 mol ice (0°C) $\xrightarrow{\Delta H_3}$ 1 mol ice (–10°C)

$\Delta H_1 = nC_p\ [H_2O(l)] \times \Delta T = 1 \times 75.3\ J\ mol^{-1}\ K^{-1} \times (0 - 10)\ K$

$= -753\ J\ mol^{-1} = -0.753\ kJ\ mol^{-1}$

$\Delta H_2 = n(\Delta_{freezing}H) = n(-\Delta_{fus}H)\ (\because \Delta_{freezing}H = -\Delta_{fus}H)$

$= 1 \times (-6.03) = -6.03\ kJ\ mol^{-1}$

$\Delta H_3 = nC_p\ [H_2O(s)]\ \Delta T = 1 \times 36.8\ J\ mol^{-1}\ K^{-1} \times (-10 - 0)\ K$

$= -368\ J\ mol^{-1} = -0.368\ kJ\ mol^{-1}$

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

$= -0.753\ kJ\ mol^{-1} - 6.03\ kJ\ mol^{-1} - 0.368\ kJ\ mol^{-1}$

$= -7.151\ kJ\ mol^{-1}$

Problem 2. Consider the reaction :

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) + 111\ kJ$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) + 394\ kJ$$

(i) In an oven using coal insufficient oxygen is supplied so that 60% of carbon is converted to CO_2 and 40% of carbon is converted to CO. Find the total heat generated when 100 kg of coal is burnt (assume coal contains 80% carbon).

(ii) Calculate the heat produced when efficient oven is used so that only CO_2 is produced.

(iii) Calculate the percentage loss in the heating value for the inefficient fuel.

Solution (i) Weight of coal = 100 kg

Weight of carbon in coal $= \frac{100 \times 80}{100} = 80$ kg

Weight of carbon converted to $CO_2 = \frac{80 \times 60}{100} = 48$ kg

Weight of carbon converted to CO $= \frac{80 \times 40}{100} = 32$ kg

Now according to reaction,

$$C(s) + O_2(g) \longrightarrow CO_2(g) + 394\ kJ.$$

12 g of carbon on combustion to CO_2 give heat = 394 kJ

48×10^3 g of carbon on combustion to CO_2 give heat

$= \frac{394 \times 48 \times 10^3}{12} = 1576 \times 10^3$ kJ

Similarly,

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) + 111\ kJ$$

12 g of carbon on combustion to CO give heat = 111 kJ

32×10^3 g of carbon on combustion to CO give heat

$= \frac{111 \times 32 \times 10^3}{12} = 296 \times 10^3$ kJ

$\therefore$ Total heat evolved = $1576 \times 10^3 + 296 \times 10^3$

$= 1872 \times 10^3$ kJ

(ii) When more efficient oven is used, only CO_2 will be formed from 80 kg of carbon :

12 g of carbon on combustion to CO_2 give heat = 394 kJ

80×10^3 g of carbon on combustion to CO_2 give heat $= \frac{394 \times 80 \times 10^3}{12} = \mathbf{2626.7 \times 10^3\ kJ}$

(iii) Percentage loss in heating value of inefficient oven may be calculated as :

Percentage loss

$= \frac{(2626.7 \times 10^3 - 1872 \times 10^3)}{2626.7 \times 10^3} \times 100 = \mathbf{28.7\ \%}$

Problem 3. The thermochemical equations for solid and liquid rocket fuels are given below :

(i) $2Al(s) + \frac{3}{2}O_2(g) \longrightarrow Al_2O_3(s)$; **$\Delta H = -1667.8$ kJ**

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; **$\Delta H = -285.9$ kJ**

(a) If equal masses of aluminium and hydrogen are used, which is better rocket fuel ?

(b) Determine ΔH for the reaction,

$$Al_2O_3(s) \longrightarrow 2Al(s) + \frac{3}{2}O_2(g)$$

Solution According to reaction (i)

$$2Al\ (s) + \frac{3}{2}O_2\ (g) \longrightarrow Al_2O_3\ (s)$$

$\Delta H = -1667.8$ kJ

Heat evolved in the combustion of (2 × 27) 54 g of Al = 1667.8 kJ

According to reaction (ii)

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)\ \Delta H = -285.9\ kJ$$

Heat evolved in the combustion of 2 g of hydrogen = 285.9 k.J

Making equal masses,

(a) Heat evolved in the combustion of 54 g of hydrogen

$= \frac{285.9 \times 54}{2} = 7719.3$ kJ

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$\therefore$ Hydrogen is a better rocket fuel because heat evolved from 54 g of H_2 is more than that from 54 g of Al.

(b) We are required to calculate ΔH for the reaction :

$$Al_2O_3(s) \longrightarrow 2Al(s) + \frac{3}{2} O_2(g) \quad \Delta H = ?$$

This is the reverse of equation (i). Therefore, ΔH for this reaction is $\Delta H = + 1667.8$ kJ.

Problem 4. A man takes a diet equivalent to 10000 kJ per day and does work, spending his energy in all forms equivalent to 12500 kJ per day. What is change in internal energy per day ? If the energy lost was stored as sucrose (1632 kJ per 100 g), how many days should it take to lose 2 kg of his weight ? (Ignore water loss).

Solution Energy taken by a man = 10000 kJ

Change in internal energy per day

$= 12500 - 10{,}000 = 2500$ kJ

The energy is lost by the man as he spends more energy than he takes.

Now 100 g of sugar corresponds to energy = 1632 kJ loss in energy

2000 g of sugar corresponds to energy

$$= \frac{1632 \times 2000}{100} = 32640 \text{ kJ}$$

$\therefore$ Number of days required to lose 2000 g of weight or 32640 kJ of energy

$$= \frac{32640}{2500} = 13 \text{ days.}$$

Problem 5. Propane (C_3H_8) is used for heating water for domestic supply. Assume that for 150 kg of hot water supply per day water must be heated from 10°C to 65°C. What moles and volume of propane in litres at S.T.P. would have to be used for heating this amount of water?
[ΔH (combustion) $C_3H_8 = -2050$ kJ and specific heat of water = 4.184×10^{-3} kJ/g].

Solution Heat used for heating water

$Q = m \times s \times \Delta T$

$= 150 \times 10^3 \times 4.184 \times 10^{-3} \times (65 - 10)$

$= 34518$ kJ

For burning 1 mol of propane heat is produced = 2050 kJ

$\therefore$ 2050 kJ heat will be given by propane = 1 mol

34518 kJ heat will be given by propane

$$= \frac{1}{2050} \times 34518$$

$= 16.84$ mol

Volume of propane used at N.T.P.

$= 16.84 \times 22.4$

$= 377.2$ L.

Problem 6. Diborane is a potential rocket fuel which undergoes combustion according to the reaction :

$$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$$

From the following data, calculate the enthalpy change for the combustion of diborane.

$$2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s) \quad \Delta H = -1273 \text{ kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -286 \text{ kJ mol}^{-1}$$

$$H_2O(l) \longrightarrow H_2O(g) \quad \Delta H = 44 \text{ kJ mol}^{-1}$$

$$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g) \quad \Delta H = 36 \text{ kJ mol}^{-1}$$

(I.I.T. 2000)

Solution The equation is:

$$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g) \quad \Delta H = ?$$

(i) $2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s)$ $\Delta H = -1273$ kJ mol^{-1}

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H = -286$ kJ mol^{-1}

(iii) $H_2O(l) \longrightarrow H_2O(g)$ $\Delta H = 44$ kJ mol^{-1}

(iv) $2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)$ $\Delta H = 36$ kJ mol^{-1}

Subtract eq. (iv) from eq. (i)

(v) $B_2H_6(g) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s) + 3H_2(g)$ $\Delta H = -1309$ kJ mol^{-1}

Multiply eq. (ii) by 3

(vi) $3H_2(g) + \frac{3}{2}O_2(g) \longrightarrow 3H_2O(l)$ $\Delta H = -858$ kJ mol^{-1}

Add $B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(l)$ $\Delta H = -2167$ kJ mol^{-1}

Multiply eq. (iii) by 3

(vii) $3H_2O(l) \longrightarrow 3H_2O(g)$ $\Delta H = 132$ kJ mol^{-1}

Add $B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$ **$\Delta H = -2035$ kJ mol^{-1}**

Problem 7. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of $CO_2(g)$, $H_2O(l)$ and propene (g) are –393.5, –285.8 and 20.42 kJ mol^{-1} respectively. The enthalpy of isomerisation of cyclopropane to propene is –33.0 kJ mol^{-1}.

Solution The given equations are:

(i) $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H = -285.8$ kJ

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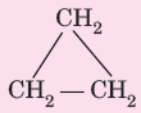
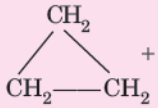
(iii) $3C(s) + 3H_2(g) \longrightarrow C_3H_6(g)\ \Delta H = 20.42$ kJ

(iv) 

$\longrightarrow C_3H_6 \qquad \Delta H = -33.0$ kJ

Cyclopropane Propene

The required thermochemical equation is

(*v*)  $+\frac{9}{2}O_2 \longrightarrow 3CO_2 + 3H_2O\ \Delta H = ?$

The required equation *(v)* can be obtained by multiplying equation *(i)* and *(ii)* by 3 and adding these, then subtracting equation *(iii)* from these and adding equation *(iv)*, *i.e.*

ΔH= [Eq. (*i*) × 3] + [Eq. (*ii*) × 3] – [Eq. (*iii*)] + [Eq. (*iv*)]

= (–393.5 × 3) + (–285.8 × 3) – (20.42) + (–33.0)

= –2091.32 kJ.

Problem 8. A gas expands from a volume of 3.0 dm^3 to 5.0 dm^3 against a constant external pressure of 3.0 atm. The work done during the expansion is used to heat 10.0 ml of water of temperature 290.0 K. Calculate the final temperature of water (specific heat of water = 4.184 J g^{-1} K^{-1}).

Solution Work done by the system,

$w = p\Delta V = p(V_2 - V_1)$

$= 3.0\ (5 - 3) = 6$ L atm.

or $w = 6 \times 101.3$ J $= 607.8$ J

(∵ 1 L atm = 101.3 J)

This work is used for heating water.

Molar heat capacity of water = 4.184 × 18 = 75.312 JK^{-1} mol^{-1}

Now, $Q = m\,s\,t$

$607.8 = 10 \times 75.312 \times t$ or $t = 0.81°$

∴ Final temperature of water = 290 + 0.81 = **290.81 K.**

Problem 9. Calculate the resonance energy of N_2O from the following data:

$\Delta H_f°$ of N_2O = 82 kJ mol^{-1}, Bond energies of N ≡ N, N = N, O = O and N = O bonds are 946, 418, 498 and 607 kJ mol^{-1} respectively.

Solution Calculate the expected value of $\Delta H_f°$ for N_2O for the reaction :

$$N{\equiv}N(g) + \frac{1}{2}\ O{=}O(g) \longrightarrow N = N = O$$

$\Delta H°$ = (Energy required to break bonds in reactants) – (Energy released in forming bonds in products)

= [B.E. (N ≡ N) + ½ B.E. (O = O)] – [B.E. (N = N) + B.E. (N = O)]

= [946 + ½ (498)] – [418 + 607]

= 1195 – 1025 = 170 kJ mol^{-1}.

$\Delta_f H°$ of N_2O = 82 kJ mol^{-1}

Resonance energy = Observed $\Delta_f H°$ – Calculated $\Delta_f H°$

= 82 – 170 = **– 88 kJ mol^{-1}**

Problem 10. An athlete is given 100 g of glucose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilizes 50% of this gained energy in the event. In order to avoid storage of energy in the body, calculate the mass of water he would have to perspire. The enthalpy of evaporation of water is 44 kJ mol^{-1}.

Solution Amount of energy given to athlete = 1560 kJ

Energy lost in the event

$$= \frac{1560 \times 50}{100} = 780 \text{ kJ}$$

Energy stored in the body =1560 – 780 = 780 kJ

For evaporation of water,

$H_2O(l) \longrightarrow H_2O(g)$

$\Delta H = 44$ kJ mol^{-1}

For consumption of 44 kJ of energy, water evaporated = 18 g

For consumption of 780 kJ of energy, water evaporated

$= \frac{18}{44} \times 780 =$ **319.1 g.**

LIMITATIONS OF FIRST LAW OF THERMODYNAMICS : SPONTANEITY

The first law of thermodynamics is concerned with the conversion of energy from one form to another. It helps us to understand energy transformation in different chemical reactions and processes. But first law of thermodynamics does not provide any information about the spontaniety or feasibility of a process. For example, the first law does not indicate whether heat can flow from a cold body to a hot body or from a hot body to a cold body. However, it is a common observation that all processes have a natural direction *i.e., a direction in which they take place of their own.*

A hot object cools down to the temperature of the surroundings but an object does not become hotter than its surroundings of its own. For example, when a cup of hot tea is kept in a room, it cools spontaneously by losing heat to the surroundings. Obviously, the first law of thermodynamics is obeyed because the energy lost by the system (*i.e.*, the cup of tea) is gained by the surroundings. However, we never observe an amusing situation where a cup of tea at room temperature

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becomes hot of its own. The first law will still be obeyed in this reverse process when the surroundings lose energy and the system gains it. But it never happens.

Similarly, a gas expands to fill the space available to it. However, it does not contract to a smaller volume of its own.

Many chemical reactions also proceed spontaneously in one direction only. For example, when we mix equal volumes of hydrochloric acid and sodium hydroxide, the neutralization reaction proceeds spontaneously forming sodium chloride and water. However, if sodium chloride is dissolved in water, the reverse reaction does not occur of its own.

Similarly, carbon burns in oxygen to give carbon dioxide spontaneously, but carbon dioxide even on strong heating does not decompose to give carbon and oxygen.

Naturally, a curious question comes to our mind ***"Why do changes take place in a particular direction?"*** The first law of thermodynamics does not determine the feasibility or spontaneity of a process. The spontaneity or feasibility of a physical or a chemical process is decided by the second law of thermodynamics as discussed below.

Spontaneity of Processes

The term spontaneity means the **feasibility of a process.** *A process which can take place by itself under the given set of conditions once it has been initiated if necessary, is said to be a* **spontaneous process.** In other words, a spontaneous process is a process that can occur without work being done on it. The spontaneous processes are also called **feasible** or **probable processes.** It may be noted that the term spontaneous should not be taken to mean that the process occurs *instantaneously.* It simply predicts that the process has natural potential to occur. The actual rate of the process may vary from very slow to extremely fast.

There are also some processes which require some initiation before they can proceed. But once initiated, they proceed by themselves. These processes are also regarded as spontaneous processes. Thus, the spontaneous processes may be of two types.

(*a*) Spontaneous processes where no initiation is needed

(*i*) Sugar dissolves in water and forms a solution

Sugar + Water $\longrightarrow$ Solution of sugar in water

(*ii*) Water keeps on evaporating from ponds, rivers, sea and open vessels

$$H_2O(l) \longrightarrow H_2O(g)$$

(*iii*) Nitric oxide (NO) and oxygen react to form nitrogen dioxide

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

(*b*) Spontaneous processes where some initiation is required

(*i*) Once a reaction between hydrogen and oxygen is initiated by passing electric spark through it, then it occurs itself spontaneously even at room temperature.

$$2H_2(g) + O_2(g) \xrightarrow{\text{Electric}} 2H_2O(l)$$

(*ii*) In domestic oven, coal (carbon) keeps on burning once initiated.

$$C(s) + O_2(g) \xrightarrow{\text{ignition}} CO_2(g)$$

(*iii*) Methane burns with oxygen once ignited.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

(*iv*) Heating of calcium carbonate to give calcium oxide and carbon dioxide is initiated by heat.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

From the above reactions, it can be concluded that the **spontaneity** (or **feasibility**) means *the inherent tendency of a process to occur of its own in a particular direction under a given set of conditions.*

On the other hand, *the processes which are forbidden and are made to take place only by supplying energy continuously from outside the system* are called **non-spontaneous processes.** In other words, non spontaneous processes can be brought about by doing work. For example, a cup of tea can be made hot (reverse of natural process) by heating. But this is not a spontaneous process because an outside agency (a gas burner) has to be used. Similarly, a gas can be compressed to a smaller volume, by applying external pressure.

There is another important feature of the spontaneous changes. These spontaneous processes proceed till an equilibrium is achieved. For example, a cup of hot tea cools until it attains the temperature of the surroundings after which no change in temperature is observed. We say that the cup of tea and the surroundings are in **thermal equilibrium.** Similarly, mixing of two gases continue until each is evenly distributed throughout both the containers. Thus, **all spontaneous changes proceed till equilibrium is achieved.**

The natural tendency of various processes to occur spontaneously leads to very **curious question** in our mind. **"What is the driving force which makes a process spontaneous ?"**

Spontaneity of a Process and Enthalpy change

It is a well known fact that all physical and chemical processes are accompanied by energy changes. Let us try to interpret various spontaneous processes on the basis of changes in energy. Think of spontaneous processes such as falling of a cricket ball from our hands to the ground; flowing of water from *higher level to lower level*. Similarly, a rock spontaneously rolls down a slope if it is dislodged. It never rolls up to the top again as shown in Fig. 16.

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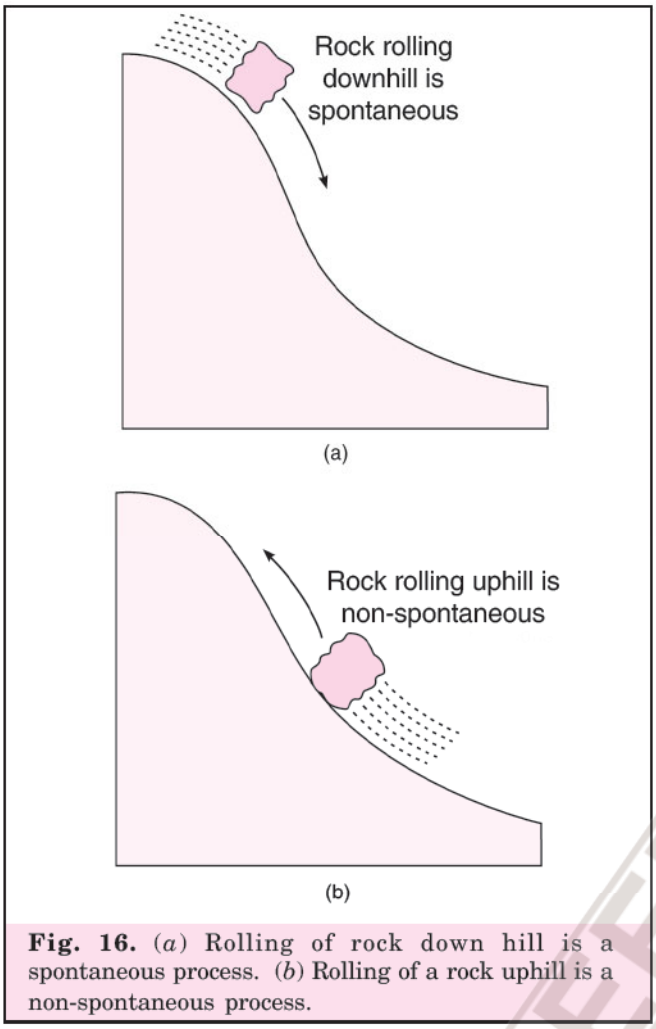

Fig. 16. (*a*) Rolling of rock down hill is a spontaneous process. (*b*) Rolling of a rock uphill is a non-spontaneous process.

We know that the ball or water or rock possesses more potential energy at higher level than at lower level. This suggests that these spontaneous processes which involve macroscopic objects proceed by decrease of energy. Moreover, *the state of lowest energy corresponds to the state of maximum stability.* Therefore, the natural tendency of all systems in this universe to go from unstability to stability supports the fact that any process which involves a decrease in energy should have an inherent tendency to take place.

Most of the spontaneous chemical reactions are also found to be exothermic. For example :

$$C(s) + O_2(g) \longrightarrow CO_2(g)\ ; \quad \Delta H = -394\ kJ\ mol^{-1}$$

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)\ ; \quad \Delta H = -92.4\ kJ\ mol^{-1}$$

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g);\ \Delta H = -184.64\ kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)\ ; \quad \Delta H = -285.7\ kJ\ mol^{-1}$$

Similarly, octane burns spontaneously in oxygen to give carbon dioxide and water and a lot of heat is evolved.

$$2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16\ CO_2(g) + 18H_2O\ (l)$$

Octane $\quad \Delta H = -10951.3\ kJ\ mol^{-1}$

Thus, *it may be concluded that all those processes which are accompanied by decrease of energy (exothermic reactions, having negative value of ΔH) occur spontaneously.* In other words, *the sign of ΔH may be taken as a criterion for the spontaneity of a process* **and decrease of enthalpy i.e. –ΔH may be regarded as the driving force behind the spontaneous processes.**

Limitations of Criterion of Decrease of Enthalpy

The criterion of decrease of enthalpy for the feasibility of chemical reactions fails to explain the following facts :

1. Endothermic reactions are also known to occur spontaneously.

There are a number of endothermic reactions (ΔH, positive), which are known to be spontaneous. A few examples of such processes are given below :

(*i*) Evaporation of water from an open container is an endothermic process but it is spontaneous in nature.

$$H_2O(l) \longrightarrow H_2O(g)\ ; \quad \Delta H = +44.0\ kJ\ mol^{-1}$$

(*ii*) Formation of nitrogen dioxide from nitrogen and oxygen :

$$\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \quad \Delta H^\circ = +33.2\ kJmol^{-1}$$

(*iii*) Reaction of carbon and sulphur to form carbon disulphide

$$C\ (graphite,s) + 2S(l) \longrightarrow CS_2\ (l) \quad \Delta H^\circ = +128.5\ kJ\ mol^{-1}$$

(*iv*) Dissolution of ammonium chloride in water is endothermic but occurs spontaneously.

$$NH_4Cl(s) \longrightarrow NH_4^+(aq) + Cl^-(aq); \quad \Delta H = +15.1\ kJ\ mol^{-1}$$

(*v*) Decomposition of mercuric oxide on heating

$$HgO(s) \longrightarrow Hg(l) + \tfrac{1}{2}O_2(g); \quad \Delta H = +90.3\ kJ\ mol^{-1}$$

(*vi*) Decomposition of dinitrogen pentoxide (N_2O_5) into NO_2 and O_2 is endothermic but occurs spontaneously

$$2N_2O_5\ (g) \longrightarrow 4NO_2\ (g) + O_2(g); \quad \Delta H = 219.0\ kJ\ mol^{-1}$$

(*vii*) Reaction between barium hydroxide and ammonium thiocyanate is spontaneous but highly endothermic.

$$Ba(OH)_2.8H_2O\ (s) + 2\ NH_4SCN\ (s) + Heat \longrightarrow Ba(SCN)_2\ (aq) + 2NH_3\ (aq) + 10\ H_2O(l)$$

2. Reactions do not go to completion.

Most of the reactions do not go to completion even though ΔH remains negative throughout. In fact, all spontaneous chemical reactions proceed only until an equilibrium is attained.

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3. Reversible reactions also occur.

Most of the reactions are reversible in nature. In these reactions both the forward and the backward reactions occur simultaneously. For example, in the following reaction, the forward reaction is *exothermic* but the backward reaction is *endothermic :*

$$H_2(g) + I_2(g) \longrightarrow 2HI(g); \qquad \Delta H = -ve$$
$$2HI(g) \longrightarrow H_2(g) + I_2(g); \qquad \Delta H = +ve$$

But both the reactions occur. This means that reactions with negative value of ΔH as well as positive value of ΔH are occurring simultaneously. It may be concluded ***that the tendency to have minimum energy i.e., –ΔH may be the criterion for a process to be spontaneous but it cannot be the only or sole criterion.***

Expansion of an ideal gas into vacuum

When an ideal gas is allowed to expand through a pinhole into vacuum, it is a spontaneous process. In this expansion, there is no energy change of the system.

According to first law of thermodynamics, the gas can lose energy only in two ways. It can either release heat to the surroundings or it can do work on them. As shown in Fig. 17, the gas chamber is insulated so that there is no loss of heat to the surroundings. Therefore, $q = 0$.

Further, there is no force which opposes the expansion and, therefore, no work is done. For this isolated system, $p_{ext} = 0$ because of vacuum, so that

$w = - p_{ext} \times \Delta V = 0$

According to first law of thermodynamics,

$\Delta U = q + w = 0 + 0$

Thus, **expansion of an ideal gas is a spontaneous process in which there is no change of energy at all.**

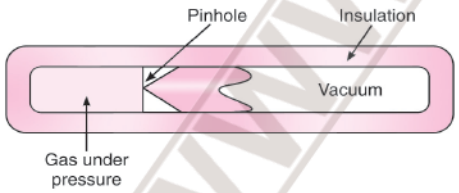

Fig. 17. Spontaneous expansion of an ideal gas into vacuum.

RANDOMNESS OR DISORDER AND SPONTANEITY

In order to find out some other factors which may be responsible for the feasibility of a process, let us examine endothermic reactions. The simplest process occurring without any energy change (*i.e.*, ΔH is almost zero) may be illustrated with the help of following experiment.

Let us consider two containers connected by means of a valve as shown in Fig. 18. The containers are perfectly insulated so that no heat enters or leaves the system. While one container is filled with a litre of helium gas, the other is filled with a litre of neon gas. The two gases are non-reacting (being inert gases). When the valve is opened, we observe that the two gases get mixed together spontaneously. During the mixing, there is a negligible energy change and, therefore, the criterion of decrease of energy for feasibility of process does not help us. If we look closely to the final and initial states of system, we observe that in the initial state the two gases are orderly filled separately in the two containers. On the other hand, after mixing, helium and neon are distributed between both the containers. In other words, each gas occupies a large volume in the final state and, thereby, number of possible locations for the molecules of each gas is increased. This means that there is **more disorder** or **randomness on mixing**. Thus, the gases mix to achieve more randomness. Once mixed the gases cannot separate because to do so they will involve decrease in randomness due to lesser volume. Thus, it may be concluded that *the process proceeds spontaneously in a direction in which the randomness or disorder of the system increases.*

Thus, the mixing of two gases is a spontaneous process. On the other hand , once mixed the gases cannot separate of its own and therefore it is a non-spontaneous process.

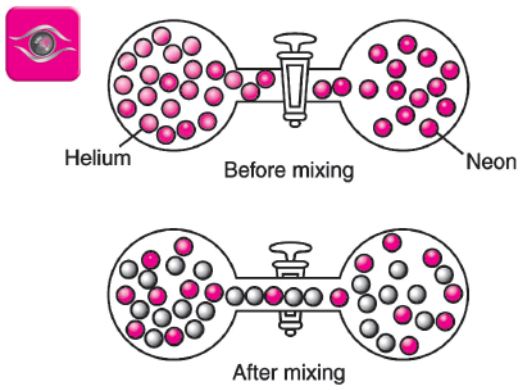

Fig. 18. Process of mixing of two gases. Gases mix spontaneously because of increase in randomness.

Some common examples of processes which occur in the direction of **increased randomness** are given below :

(*i*) *Conversion of solids into liquids.* The melting of solids into liquids (ΔH, +ve) results in the increase of randomness.

$$H_2O(s) \longrightarrow H_2O(l)$$

(*ii*) *Evaporation of water.* The evaporation of water also results into increase of randomness because the

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molecules in the vapour state have more randomness than in the liquid state.

$$H_2O(l) \longrightarrow H_2O(g)$$

(*iii*) *Dissolution of ammonium chloride in water.* Solid ammonium chloride has less randomness while in solution ammonium chloride particles move freely as NH_4^+ and Cl^- ions and hence, randomness increases.

$$NH_4Cl(s) + \text{Water} \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

Thus, we find that in all the above endothermic processes, there is always a tendency for the system to become more **disordered or chaotic.** Since the above reactions are spontaneous, *the tendency to achieve maximum randomness or disorder is another factor which determines the spontaneity of a process.*

Driving Force as the Overall Tendency for a Process

We have learnt that the spontaneous processes occur because of the two tendencies :

(*i*) *Tendency of a system to acquire a state of minimum energy* (E).

(*ii*) *Tendency of a system to acquire a state of maximum randomness* (R).

The overall tendency for a process to take place by itself is called the **driving force.**

Regarding these two tendencies it is very important to keep in mind the following points :

(*i*) *The two tendencies act independent of each other.*

(*ii*) *The two tendencies may work in the same or in opposite directions in a process.*

Thus,

- When there is no change in energy the second tendency is the governing factor *i.e.,* reaction will be spontaneous or non-spontaneous depending upon whether randomness factor favours or opposes.
- When there is no change in randomness, the energy factor is the controlling factor.

However, this is not so simple in actual practice as both the tendencies operate simultaneously. In these cases, the significance of the magnitude of these tendencies becomes important. Obviously, *the tendency with the greater magnitude determines whether the process is feasible or not.*

For example, the reaction will be feasible in the forward direction under the following conditions:

(*i*) When both E and R favour the forward reaction.

E ⇨
R ⇨
D ⇨ Feasible in forward direction

(*ii*) When E favours, R opposes but E > R.

E ⇨
R ⇦
D ⇨ Feasible in forward direction

(*iii*) When E opposes, R favours but E < R.

E ⇦
R ⇨
D ⇨ Feasible in forward direction

However, the reaction will not be feasible in the forward direction under the following conditions:

(*iv*) When E favours, R opposes but E = R.

E ⇨
R ⇦
D = 0 At equilibrium

(*v*) When E opposes, R favours but E = R.

E ⇦
R ⇨
D = 0 At equilibrium

(*vi*) When E favours, R opposes but E < R.

E ⇨
R ⇦
D ⇦ Not feasible in forward direction

(*vii*) When E opposes, R favours but E > R.

E ⇦
R ⇨
D ⇦ Not feasible in forward direction

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It may be noted that in (*iv*) and (*v*) cases, the reaction will be at equilibrium and in (*vi*) and (*vii*) cases, the reaction will be spontaneous in the backward direction.

ENTROPY AND SPONTANEITY

The extent of disorder or randomness in a system may be expressed by a thermodynamic property known as **entropy. Entropy** may be defined as

the property of a system which measures the degree of disorder or randomness in the system.

It is generally expressed by the symbol, S. Entropy like internal energy and enthalpy, is a ***state function*** and change in entropy, therefore, depends only on the initial and final states of the system. The change in entropy during the process when a system undergoes a change from one state to another is represented by ΔS. Thus,

$$\Delta S = S \text{ (final state)} - S \text{ (initial state)}$$

and for chemical reactions,

$$\Delta S = S \text{ (products)} - S \text{ (reactants)}$$

For chemical reactions, entropy change is attributed to the change in rearrangement of atoms or ions in the reactants to that in the products. If the structure of the products is very much disordered than that of the reactants, there will be resultant increase in entropy (ΔS = + ve). Therefore, change in entropy accompanying a chemical reaction may be estimated quantitatively by the consideration of the structures of species taking part in the reaction and the structures of the products formed.

Entropy may also be related to the heat involved in a process. Whenever heat is added to the system, it increases molecular motion resulting increased randomness in the system. The distribution of heat also depends on the temperature at which heat is added to the system. A system at a higher temperature has greater randomness in it than at lower temperature. *Thus,* ***temperature is also a measure of average chaotic motion or randomness of particles in the system.*** When heat is added to a system at lower temperature, it increases the randomness of the system to greater extent than when the same quantity of heat is added to it at a higher temperature. This suggests that entropy change is inversely proportional to the temperature.

For a reversible process at equilibrium, the change in entropy may be expressed as :

$$\Delta S = \frac{q_{rev}}{T} \qquad ...(i)$$

where q_{rev} represents the heat absorbed when the process is carried out reversibly and isothermally *i.e.,* at constant temperature. Thus, **entropy change during a process may also be defined as the amount of heat absorbed isothermally and reversibly divided by the absolute temperature at which heat is absorbed.**

The ΔS defined by Eq. (*i*) is independent of path because it is a state function.

Units of entropy. Since entropy change is expressed as heat divided by temperature, the units of entropy are calories per degree (expressed as entropy units **eu**) or **joules per kelvin per mole,** $JK^{-1}\,mol^{-1}$.

KEY NOTE

It may be noted that q_{rev}/T is a measure of increase in disorder of the system. This can be easily justified. When energy is absorbed by the system, it leads to vigorous movement of the molecules due to increased kinetic energy. In other words, the heating stimulates the thermal motion of the molecules. As a result, disorder in the system increases. The more heat the system absorbs, the more disordered it becomes. However, if heat is absorbed at low temperature, it becomes more disordered than when the same amount of heat is added at higher temperature. This justifies the temperature (T) in denominator in Eq. (*i*). Thus, **there is large increase in entropy when a lot of energy is transferred to a system at a low temperature.**

Physical Meaning of Entropy

The physical meaning of entropy is that entropy is a measure of degree of disorder (or randomness) of a system. The relation between entropy and disorder provides a suitable explanation for entropy change in various processes. The greater the disorder in a system, the higher is the entropy. Obviously, for a given substance the solid state is the state of lowest entropy (most ordered state), the gaseous state is the state of highest entropy and the liquid state is intermediate between the two.

Thus, when a sample changes from solid to liquid to gas, its particles become increasingly disordered and, therefore, its entropy increases. This is shown in Fig. 19.

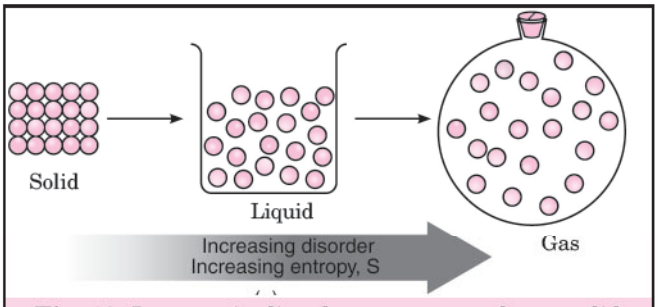

Fig. 19. Increase in disorder or entropy when a solid changes to liquid to gas.

Similarly, in the case of mixing of two gases when the stop cork is opened, the gases mix to achieve more randomness or disorder. In this case, there is no

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exchange of matter or energy between the system and the surroundings. The change occurs from ordered state (less entropy) to disordered state (higher entropy). Thus, the change in entropy is positive.

Entropy as a state function

Consider a system consisting of a cylinder containing a gas fitted with a frictionless and weightless piston which is in contact with a large heat reservoir. Let us consider isothermal and reversible expansion of the gas from volume V_1 to V_2 and the substance absorbs heat q, at temperture T.

$$\therefore \text{ Change in entropy of the system, } \Delta S_{sys} = \frac{q_{rev}}{T}$$

Since an equivalent amount of heat is lost by the reservoir and therefore, change in entropy of reservoir will be :

$$\Delta S_{reservoir} = -\frac{q_{rev}}{T}$$

Minus sign indicates that heat is lost by the reservoir to the system.

Total entropy change may be written as :

$$\Delta S_1 = \Delta S_{sys} + \Delta S_{res}$$

$$= \frac{q_{rev}}{T} + \frac{(-q_{rev})}{T} = 0$$

Now, let us assume that we compress the gas thermally from a volume of V_2 to V_1 so that heat is given by the system is $-q_{rev}$

$$\therefore \text{ Change in entropy of the system, } \Delta S_{sys} = -\frac{q_{rev}}{T}$$

Since reservoir has gained heat, change in entropy of reservoir is

$$\Delta S_{reservoir} = \frac{q_{rev}}{T}$$

Total change in entropy is :

$$\Delta S_2 = \Delta S_{sys} + \Delta S_{rev}$$

$$= \frac{-q_{rev}}{T} + \frac{q_{rev}}{T} = 0$$

Thus, the total entropy change for the complete cycle is zero, i.e.,

$\Delta S_1 + \Delta S_2 = 0$. In other words, after the end of cycle, the entropy of the system is same as it had initially. Therefore, **entropy is a state function.**

As we have studied, the total entropy change (ΔS_{total}) of system and surroundings of a spontaneous process is given as :

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0$$

As we have learnt, in an isolated system such as mixing of gases, there is no exchange of energy or matter between the system and the surroundings. But due to increase in randomness, there is increase in entropy. Thus, we can say that for a spontaneous process in an isolated system, the change in entropy is positive *i.e.*, $\Delta S > 0$. However, if the system is not isolated, we have to take into account the entropy changes of the system and the surroundings. Then, the total entropy change (ΔS_{total}) will be equal to the sum of the change in entropy of the system (ΔS_{sys}) and the change in entropy of the surroundings (ΔS_{surr}) *i.e.*,

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

For a spontaneous process, ΔS_{total} must be positive *i.e.*,

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0 \qquad ...(ii)$$

But system and surroundings constitute *universe* for thermodynamic point of view so that for spontaneous change

$$\Delta S_{universe} > 0$$

This led to the formulation of second law of thermodynamics.

STATEMENT OF SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics states that

the entropy of the universe always increases in the course of every spontaneous (natural) change.

Thus, combining the first and second laws of thermodynamics, the combined statement becomes :

the energy of the universe is conserved whereas the entropy of the universe always increases in any natural process.

Entropy and Equilibrium State

During a spontaneous process, the entropy of the system goes on increasing. When the system reaches the equilibrium state, the entropy of the system becomes maximum and, therefore, no more increase in the entropy of the system is possible. Thus, the condition for any system to achieve equilibrium state is that its entropy becomes maximum. The mathematical condition for entropy (S) to be maximum is that the change in entropy (ΔS) is zero *i.e.*,

$$\Delta S = 0 \text{ (at equilibrium)}$$

ENTROPY AND SPONTANEITY OF A REACTION

From the above discussion, we may conclude that

(*i*) if ΔS_{total} is positive, the process is **spontaneous.**

(*ii*) if ΔS_{total} is negative, the forward process is non-spontaneous; the **reverse process may be spontaneous**.

(*iii*) if ΔS_{total} is zero, the process is in **equilibrium**.

Let us apply the entropy criterion to decide the feasibility of the process of conversion of water to ice, at 1 atm pressure,

$$H_2O(l) \longrightarrow H_2O(s)$$

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The entropy changes for three different temperatures 272, 273 and 274 K are given in Table 9.

Table 9. Entropy changes for the transformation : $H_2O(l) \longrightarrow H_2O(s)$ at 1 atm. pressure

Temperature °C	Temperature K	ΔS sys (JK^{-1} mol^{-1})	ΔS surr. (JK^{-1} mol^{-1})	ΔS total (JK^{-1} mol^{-1})
–1	272	–21.85	+ 21.93	+ 0.08
0	273	–21.99	+ 21.99	0.00
+1	274	–22.13	+ 22.05	–0.08

(*i*) At 272 K,

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$
$$= -21.85 + 21.93 = +0.08\ JK^{-1}\ mol^{-1}$$

Since ΔS_{total} is positive at 272 K, the freezing of liquid water to ice is spontaneous.

$H_2O(l) \longrightarrow H_2O(s)$ **Spontaneous at 272 K**

(*ii*) At 274 K

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$
$$= -22.13 + 22.05 = -0.08\ JK^{-1}\ mol^{-1}$$

Since ΔS_{total} is negative, the freezing of water is not spontaneous at 274 K.

$H_2O(l) \longrightarrow H_2O(s)$

Non-spontaneous at 274 K

But for the reverse process, ΔS_{total} will be positive *i.e.*, $\Delta S_{total} = +0.08\ JK^{-1}\ mol^{-1}$ *i.e.*, melting is spontaneous at 274 K.

$H_2O(s) \longrightarrow H_2O(l)$

Spontaneous at 274 K

(*iii*) At 273 K

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$
$$= -21.99 + 21.99 = 0$$

Since ΔS_{total} is zero, the process is at equilibrium *i.e.,* neither freezing nor melting is spontaneous. At this temperature, water and ice are in equilibrium and no net change is observed.

$H_2O(l) \longrightarrow H_2O(s)$

Equilibrium at 273 K

SOLVED EXAMPLES

❑ Example 52.

Calculate the entropy change in surroundings when 1.00 mol of H_2O (l) is formed under standard conditions.

$\Delta_f H^\circ = -286\ kJ\ mol^{-1}$ **N.C.E.R.T.**

Solution: The standard enthalpy of formation of water at 298K $= -286 kJ\ mol^{-1}$

The reaction is exothermic so heat gained by surroundings, $\Delta H_{sur} = 286.0\ kJmol^{-1}$

$$\Delta S_{sur} = \frac{286.0 \times 10^3\ Jmol^{-1}}{298\,K}$$
$$= 959.73\ JK^{-1}$$

Thus, we observe ΔS_{total} is a criterion for spontaneity of a change.

Characteristics of Entropy

The important characteristics of entropy are summed up below :

1. Entropy is an extensive property. Its value depends upon the amount of the substance present in the system.
2. Entropy of a system is a state function. It depends upon the state variables (T, *p*, V, *n*). Thus, the change in entropy is given as :
$$\Delta S = S_{final\ state} - S_{initial\ state}$$
3. The change in entropy in going from one state to another is independent of the path.
4. The change in entropy for a cyclic process is always zero.
5. The total entropy change of an isolated system is equal to the entropy change of system and entropy change of the surroundings. The sum is called **entropy change of universe**.
$$\Delta S = \Delta S_{sys} + \Delta S_{surr}$$
6. In a reversible process, $\Delta S_{universe} = 0$ and, therefore,
$$\Delta S_{sys} = -\Delta S_{surr}$$
7. In a irreversible process, $\Delta S_{universe} > 0$. This means that there is increase in entropy of universe in spontaneous changes.

❑ Example 53.

Predict in which of the following entropy increases / decreases :

(*a*) $H_2(g) \longrightarrow 2H(g)$

(*b*) $2\ NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

(*c*) *A liquid crystallizes into a solid.*

(*d*) *Temperature of a crystalline solid is raised from 0 K to 115 K.* **N.C.E.R.T.**

Solution : (*a*) One molecule of H_2 gives two atoms. Therefore, the number of particles increases leading to more disordered state. Thus, **entropy increases**.

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(*b*) Reactant $NaHCO_3$ is a solid and it changes to one solid and two gases. Therefore, products have higher entropy and hence **entropy increases.**

(*c*) After crystallisation, solid has more ordered state and less **entropy.** Hence **entropy decreases.**

(*d*) At 0 K, the crystalline solid has most ordered state. When temperature increases to 115 K, molecules begin to move and ordered arrangement decreases. Therefore, **entropy increases.**

❑ **Example 54.**

Consider the reaction for the dissolution of ammonium nitrate :

$NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$

$\Delta H = +28.1\ kJ\ mol^{-1}$, $\Delta S = 108.7\ J\ K^{-1}mol^{-1}$.

Calculate the change in entropy of the surroundings and predict whether the reaction is spontaneous or not at 25°C ?

Solution : The reaction is endothermic, $\Delta H = 28.1\ kJ\ mol^{-1}$

$\therefore$ Entropy change in surroundings

$$\Delta S_{sur} = -\frac{\Delta H_{sys}}{T}$$

$$= -\frac{28.1 \times 10^3}{298}$$

$$= -94.3\ JK^{-1}\ mol^{-1}$$

$$\Delta S_{sys} = 108.7\ JK^{-1}\ mol^{-1}$$

$\therefore$ $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$

$= 108.7 - 94.3$

$= 14.4\ JK^{-1}\ mol^{-1}$

There is increase in total entropy so ammonium nitrate dissolves spontaneously.

❑ **Example 55.**

The oxidation of iron occurs as :

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

The enthalpy of formation of $Fe_2O_3(s)$ is – 824.2 kJ mol^{-1} and entropy change for the reaction is – 549 JK^{-1} mol^{-1} at 298 K. Inspite of negative entropy change of this reaction, why is the reaction spontaneous at 298 K ? ***N.C.E.R.T.***

Solution : For the reaction :

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

$\Delta_r H = 2\ \Delta_f H\ (Fe_2O_3) = 2 \times -824.2 = -1648.4\ kJ$

To calculate Δ_{sur}, we have to consider the heat absorbed by the surroundings which is equal to $-\Delta_r H^\circ$

Entropy change of the surroundings is (at constant pressure),

$$\Delta S_{sur} = -\frac{\Delta H_{sys}}{T}$$

$$= -\frac{-1648.4 \times 10^3\ J}{298\ K}$$

$$= 5531\ JK^{-1}$$

Now, total entropy change is

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{sur}$$

$$= -549 + 5531$$

$$= +4982\ JK^{-1}\ mol^{-1}$$

Since there is increase in entropy (ΔS_{total}= +ve), the oxidation of iron is spontaneous process.

ENTROPY CHANGES DURING PHASE TRANSITION

The change of matter from one state (solid, liquid or gas) to another is called **phase transition.** Such changes occur at definite temperatures such as melting point (solid to liquid), boiling point (liquid to vapours) etc., and are accompanied by absorption or evolution of heat.

The entropy change for these may be calculated as:

$$\Delta_{trans} S = \frac{q_{rev}}{T}$$

where q_{rev} is the heat evolved or abosrbed during transition and T is the temperature. For the transformation of one mole of a substance at constant pressure, q_{rev} is equal to molar enthalpy change for that transformation *i.e.* $q_{rev} = \Delta_{trans}H$. Let us consider different types of phase transitions :

1. Entropy of fusion

Entropy of fusion may be defined as ***the entropy change when 1 mole of the solid substance changes into liquid form at its melting point.*** For example, when ice melts as :

$$\text{Water}\ (s) \rightleftharpoons \text{Water}\ (l)$$

The change in entropy is given by

$$S^\circ_{water} - S^\circ_{ice} = \Delta_{fus}S^\circ = \frac{\Delta_{fus}H^\circ}{T_f}$$

where $\Delta_{fus}H^\circ$ is the enthalpy of fusion and T_f is the fusion temperature.

For example, the standard enthalpy of fusion, $\Delta_{fus}H^\circ$ at 273 K and 1 bar pressure for water is 6.0 kJ mol^{-1}.

$H_2O(s) \longrightarrow H_2O(l)$ $\qquad \Delta_{fus}H^\circ = 6.0\ kJ\ mol^{-1}$

$$\therefore\ \Delta_{fus}S^\circ = \frac{q_{rev}}{T} = \frac{\Delta_{fus}H^\circ}{T_f}$$

$$= \frac{6.0 \times 10^3\ J\ mol^{-1}}{273\ K}$$

$$= 21.98\ J\ K^{-1}\ mol^{-1}$$

2. Entropy of vaporisation

Entropy of vaporisation may be defined as ***the entropy change when 1 mole of a liquid changes into vapours at its boiling point.*** The entropy of vaporisation for a liquid at its boiling point is :

$$\Delta_{vap}S^\circ = \frac{\Delta_{vap}H^\circ}{T_b}$$

where $\Delta_{vap}H^\circ$ is the standard enthalpy of vaporisation and T_b is the boiling point.

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For example, standard enthalpy of vaporisation at 373 K (at 1 bar) is 40.79 kJ mol^{-1}.

$H_2O\ (l) \longrightarrow H_2O\ (g) \quad \Delta_{vap}H^\circ = 40.79\ kJ\ mol^{-1}$

$$\therefore \quad \Delta_{vap}S^\circ = \frac{\Delta_{vap}H^\circ}{T}$$

$$= \frac{40.79 \times 10^3\ J\ mol^{-1}}{373\ K}$$

$$= 109.356\ JK^{-1}\ mol^{-1}$$

3. Entropy of sublimation

Sublimation is a direct conversion of a solid into its vapour. **Entropy of sublimation** may be defined as ***the entropy change when 1 mole of a solid changes into vapour at a particular temperature.*** The entropy of sublimation at a particular temperature is

$$\Delta_{sub}S^\circ = \frac{\Delta_{sub}H^\circ}{T}$$

where $\Delta_{sub}H^\circ$ is the standard enthalpy of sublimation at the temperature T.

$$(\Delta_{sub}H^\circ = \Delta_{fus}H^\circ + \Delta_{vap}H^\circ).$$

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Example 56.

The standard enthalpy change for the transition of liquid water to steam is 40.8 kJ mol^{-1} at 373 K. Calculate the entropy of vaporisation of water.

Solution : The entropy change when liquid water changes to steam is :

$$\Delta_{vap}S^\circ = \frac{\Delta_{vap}H^\circ}{T}$$

$\Delta_{vap}H^\circ = 40.8\ kJ\ mol^{-1}$, $T = 373\ K$

$$\therefore \quad \Delta_{vap}S^\circ = \frac{40.8 \times 10^3\ J\ mol^{-1}}{373\ K} = \mathbf{109.4\ JK^{-1}\ mol^{-1}.}$$

Example 57.

Calculate the enthalpy of vaporisation per mole for ethanol. Given $\Delta S = 109.8\ JK^{-1}\ mol^{-1}$ and boiling point of ethanol = 78.5°C.

Solution : The entropy change for vaporisation,

$$\Delta_{vap}S^\circ = \frac{\Delta_{vap}H^\circ}{T_b^\circ}$$

or $\Delta_{vap}H^\circ = \Delta_{vap}S^\circ \times T_b^\circ$

$\Delta S^\circ = 109.8\ JK^{-1}\ mol^{-1}$, $T_b^\circ = 273 + 78.5 = 351.5\ K$

$\therefore \Delta_{vap}H^\circ = (109.8\ JK^{-1}\ mol^{-1}) \times (351.5\ K)$

$= 38595\ J\ mol^{-1} = \mathbf{38.595\ kJ\ mol^{-1}}.$

Example 58.

The enthalpy of vaporisation of liquid diethyl ether $(C_2H_5)_2O$ is 26.0 kJ mol^{-1} at its boiling point (35.0°C). Calculate ΔS° for the conversion of

(a) liquid to vapour and

(b) vapour to liquid at 35°C

Solution : (*a*) For vapourisation of diethyl ether :

$$\therefore \Delta_{vap}S^\circ = \frac{\Delta_{vap}H^\circ}{T}$$

$\Delta_{vap}H^\circ = 26.0\ kJ\ mol^{-1}$, $T = 273 + 35 = 308\ K$

$$\therefore \Delta_{vap}S^\circ = \frac{26.0 \times 10^3\ J\ mol^{-1}}{308\ K} = \mathbf{84.4\ JK^{-1}\ mol^{-1}.}$$

(*b*) The conversion of vapour into liquid is condensation. The enthalpy of condensation is negative of enthalpy of vaporisation.

$\Delta_{vap}H^\circ = -\Delta_{cond}H^\circ$

∴ For condensation of diethyl ether (i.e., conversion of vapour to liquid)

$$\Delta_{cond}S^\circ = \frac{\Delta_{cond}H^\circ}{T} = \frac{-26.0 \times 10^3\ mol^{-1}}{308}$$

$$= \mathbf{-84.4\ JK^{-1}\ mol^{-1}.}$$

ENTROPY CHANGES FOR AN IDEAL GAS

Entropy change (ΔS) of an ideal gas with change in *p*, V and T may be derived as :

$$\Delta S = nC_V\ ln\ \frac{T_2}{T_1} + nR\ ln\ \frac{V_2}{V_1}$$

$$\Delta S = nC_p\ ln\ \frac{T_2}{T_1} + nR\ ln\ \frac{p_1}{p_2}$$

For isothermal process, $T_1 = T_2$

$$\therefore\ \Delta S\ (\text{isothermal}) = nC_V\ ln\ \frac{T_2}{T_1} = nR\ ln\ \frac{p_1}{p_2}$$

For isochoric process (volume constant)

$$\Delta S\ (\text{isochoric}) = nC_V\ ln\ \frac{T_2}{T_1}$$

For isobaric process (pressure constant)

$$\Delta S\ (\text{isobaric}) = nC_p\ ln\ \frac{T_2}{T_1}$$

GIBBS ENERGY AND GIBBS ENERGY CHANGE AND SPONTANEITY

We have learnt that for a system, it is the total entropy change, ΔS_{total} which helps to decide the spontaneity of a process. However, most of the chemical reactions are either closed systems or open systems. Therefore, for most of the chemical reactions, there are changes in both enthalpy and the entropy. It is not possible to predict the spontaneity of a reaction on the basis of decrease in enthalpy or increase in entropy alone. For this purpose to predict the spontaneity of a chemical reaction, a new **function** known as **Gibbs energy** or **Gibbs function** is defined.

Gibbs energy of a system is defined as

the maximum amount of energy available to a system during a process that can be converted into useful work.

In other words, it is a thermodynamic quantity which is a measure of capacity of a system to do useful work. It is denoted by symbol G and is given by

$$G = H - TS$$

where H is the enthalpy of the system, S is its entropy

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and T is the absolute temperature. Gibbs energy is also called as Gibbs function. It is **extensive property and a state function.**

It may be noted that in earlier literature, G was called Gibbs free energy. But in accordance with IUPAC recommendations, it is called Gibbs energy. We shall use the term Gibbs energy in the present chapter in accordance with IUPAC recommendations.

Now, $H = U + pV$

$G = U + pV - TS$

Gibbs energy change. The change in Gibbs energy of the system may be expressed as

$\Delta G_{sys} = \Delta H_{sys} - \Delta(TS)_{sys}$

$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} - S_{sys}\,\Delta T$

At constant temperature, $\Delta T = 0$ so that

$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$

Usually the subscript 'sys' is dropped and we simply write as similarly

or $\Delta G = \Delta H - T\Delta S$ ...(*iii*)

This equation is called **Gibbs Helmholtz equation** and is very useful in predicting the spontaneity of a process. This takes into account both the terms together for spontaneity *i.e.,* energy factor (in terms of ΔH) and entropy factor (ΔS, a measure of disorder).

Units of ΔG

Dimensionally if we analyse we see that ΔG has the units of energy (i.e. kJ mol^{-1} or J mol^{-1}) because both ΔH and $T\Delta S$ are energy terms :

$\Delta G(J\ mol^{-1}) = \Delta H\ (J\ mol^{-1}) - T\Delta S\ (K\ JK^{-1}\ mol^{-1})$

GIBBS ENERGY CHANGE FOR PREDICTING FEASIBILITY OF A REACTION

We have already studied that the total entropy change, ΔS_{total} determines the spontaneity of a process. The total entropy change during a process is given by

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} \quad ...(iv)$$

If the system is in thermal equilibrium with the surroundings, then the temperature of the surroundings is the same as that of the system. Therefore, increase in enthalpy of the surroundings is equal to decrease in enthalpy of the system. Since the reaction is carried out at constant temperature and pressure heat evolved is equal to enthalpy change, i.e,

$$q_{sys} = \Delta H_{sys}$$

Now, if a reaction is conducted at constant temperature and pressure and heat (q) is given out to the surroundings reversibly, then

$$(q_p)_{surr} = -(q_p)_{sys} = -\Delta H_{sys}$$

(minus sign before q_p indicates that the heat is given out or lost to the surroundings)

The entropy change of the surroundings is :

$$\Delta S_{surr} = \frac{(q_p)_{surr}}{T} = \frac{-\Delta H_{sys}}{T} \quad ...(v)$$

Substituting Eq. (*v*) in Eq. (*iv*), we get :

$$\Delta S_{total} = \Delta S_{sys} + \left(-\frac{\Delta H_{sys}}{T}\right) \quad ...(vi)$$

Multiplying both sides by T,

$T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys}$

$-T\Delta S_{total} = \Delta H_{sys} - T\Delta S_{sys}$

From Eq. (*iii*), $\Delta H - T\Delta S = \Delta G$

$\Delta G_{sys} = -T\Delta S_{total}$

We have learnt that for spontaneous chemical changes, ΔS_{total} is positive so that

ΔG = –ve for spontaneous chemical changes.

Thus, the spontaneity of a chemical change can be predicted either by

(*i*) $T\Delta S$ system = +ve or

(*ii*) ΔG = –ve.

The use of Gibbs energy change has the advantage because it refers to system only whereas in considering entropy criteria, we have to consider the system as well as the surroundings.

Predicting Spontaneity of a Process in Terms of ΔG

The Gibbs energy change, ΔG provides the overall criterion for the feasibility of a chemical process. It gives the balance of the two tendencies, ΔH and $T\Delta S$ as :

$$\Delta G = \Delta H - T\Delta S$$

Even, if the reaction is not favoured energetically (endothermic reaction), the driving force may be provided by a favourable change in entropy. It can be shown that only those processes are spontaneous or feasible in which free energy undergoes a decrease *i.e.,* ΔG is negative. By calculating ΔH and $T\Delta S$ and hence ΔG, we can easily predict whether reaction is spontaneous or not.

1. When energy and entropy factors are favourable *i.e.,* ΔH is negative and $T\Delta S$ is positive, then ΔG *must be negative.*

i.e., $\Delta G = (-) - (+) = -ve$

Thus, ΔG *is* **negative** *for a spontaneous process.*

2. If both the tendencies oppose, *i.e.,* ΔH is positive and $T\Delta S$ is negative, then ΔG is positive.

i.e., $\Delta G = (+) - (-) = +ve$

Thus, ΔG *is* **positive** *for a non-spontaneous process.*

3. If both the tendencies are equal and opposite, for example, if ΔH is positive (unfavourable) and $T\Delta S$ is also positive (favourable) or *vice-versa* and both are of equal magnitude, then ΔG becomes zero. At this stage, *the process does not proceed in either direction and the reaction, is said to be in* **equilibrium state.**

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In short, we can say

(i) If ΔG is negative, *the process is* **spontaneous.**

(ii) If ΔG is zero, *the process is in* **equilibrium state.** *There is no net reaction in either direction.*

(iii) If ΔG is positive, *the process* **does not occur** *in the forward direction. It may, however, go in the reverse direction.*

Thus, if a change is to be spontaneous in the forward direction, ΔG must be negative.

Conditions for Spontaneity of a Process or ΔG to be Negative

ΔG would be negative under the following conditions :

(*i*) Both the energy and the entropy factors are favourable and may have any magnitude, *i.e.,* ΔH is negative and TΔS is positive.

(*ii*) When energy factor favours the change (ΔH = –ve), but entropy factor opposes the change (TΔS = –ve), then the magnitude of ΔH should be more than that of TΔS.

$$\Delta H(-ve) > T\Delta S(-ve)$$

(*iii*) When energy factor is not favouring (ΔH = +ve) but entropy factor favours the change (TΔS = + ve), then the magnitude of TΔS should be more than that of the energy factor.

$$T\Delta S\ (+ve) > \Delta H\ (+ve)$$

These conditions are summed up in Table 10.

Table 10. Conditions for spontaneous processes i.e. ΔG negative.

ΔH	TΔS	Magnitude of the tendencies
– (Favourable)	+ (Favourable)	Any magnitude
– (Favourable)	– (Unfavourable)	ΔH > TΔS
+ (Unfavourable)	+ (Favourable)	TΔS > ΔH

Effect of Temperature on Feasibility of a Process

As is evident from equation : ΔG = ΔH – TΔS ; the term TΔS may assume larger values at higher temperatures due to increase in multiplying factor T as well as increase in randomness. But the other factor ΔH does not vary appreciably with temperature. Therefore, the Gibbs energy change (overall tendency) of a process to take place, is also influenced by the temperature. The effect of temperature is different for exothermic and the endothermic reactions as discussed below.

(a) Exothermic Reactions

For exothermic reactions, ΔH is always negative, and, therefore, it is favourable. Now TΔS can have either positive or negative value.

(*i*) If TΔS is positive *i.e.,* favourable, then ΔG can have only negative value and the *process is spontaneous at all temperatures.*

For example, in combustion of carbon at 298 K

$$C\ (graphite) + O_2\ (g) \longrightarrow CO_2\ (g)$$

$$\Delta_r H^\circ = -393.5\ kJ\ mol^{-1}$$

The entropy of reaction, $\Delta_r S^\circ = 0.0029\ kJ\ mol^{-1}$ so that

$$\Delta_r G^\circ = -393.5 - 298\ (0.0029)$$
$$= -394.36\ kJ\ mol^{-1}$$

In this case, $\Delta_r G^\circ$ is always negative and therefore, the reaction is always spontaneous.

(*ii*) If TΔS is negative *i.e.,* unfavourable. The value of ΔG will be negative only if ΔH > TΔS. *This fact will be more predominant at lower temperatures* which makes the contribution of TΔS (opposing factor) less. When temperature is very high, –TΔS will have large magnitude and ΔG will be positive and as such the process may not be spontaneous. But as *the temperature is lowered,* then the TΔS value decreases so that its unfavourable influence is reduced. At very low temperature, the value of ΔH may become greater than the small value of TΔS and thus, ΔG becomes negative and the process is spontaneous under these conditions. Hence, *exothermic reactions are favoured by decreasing temperature.*

These reactions are also called **enthalpy driven**. For example, in combustion of methane (CH_4), the reaction is spontaneous because of large negative value of ΔH at 298 K.

$$CH_4\ (g) + 2O_2\ (g) \longrightarrow 2\ H_2O\ (l) + CO_2\ (g)$$

$$\Delta_r H^\circ = -890.3\ kJ\ mol^{-1}$$

$\Delta_r S^\circ$ for the reaction has been found to be $-0.2430\ kJ\ mol^{-1}\ K^{-1}$ so that

$$\Delta_r G^\circ = -890.3 - 298\ (-0.2430)$$
$$= \mathbf{-817.89\ kJ\ mol^{-1}.}$$

This reaction is also spontaneous at 298 K.

Thus,

▶ **An exothermic reaction which may be non-spontaneous at high temperature because of unfavourable entropy factor may become spontaneous at low temperature.**

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(b) Endothermic Reactions

For endothermic reactions, ΔH is positive and always opposes the process. Now

(*i*) If TΔS is negative and opposes the process, then ΔG will be positive and the *process is always non-spontaneous.*

(*ii*) On the other hand, when TΔS is positive (favourable) the value of ΔG will be negative only if TΔS > ΔH. *This fact will be more predominant at higher temperatures* which makes the contribution of TΔS (favouring factor) more. *At low temperature,* TΔS may have small value and therefore, ΔH may be greater than TΔS. Under these conditions, ΔG may be positive and the reaction may not be spontaneous at low temperature. *As temperature is increased,* the term TΔS increases while ΔH does not change appreciably. Hence at high temperature, the magnitude of TΔS will be quite large and will be more than ΔH so that ΔG becomes negative. This means that *endothermic reactions are favoured by increasing temperature.*

Thus,

▶ ***An endothermic reaction which may be non-spontaneous at low temperature because of unfavourable entropy factor may become spontaneous at high temperature.***

These results are summed up in Table 11.

Table 11. Tendencies of reactions to occur in the forward direction and effect of temperature.

Reaction	Sign of ΔH	Sign of TΔS	Sign of ΔG	Behaviour
Exothermic	–	+	–	Spontaneous
	–	–	– at low T	Spontaneous
			+ at high T	Non-spontaneous
Endothermic	+	–	+	Non-spontaneous
	+	+	+ at low T	Non-spontaneous
			– at high T	Spontaneous

Thus, temperature plays an important role in deciding the spontaneity of a reaction. A reaction may not be spontaneous at low temperature but it becomes spontaneous at high temperature and vice versa. For example, consider the melting of ice into water,

$$\text{Ice}(s) \longrightarrow \text{Water}\ (l)$$

The data at three temperatures 263 K, 273 K and 283 K are given below :

Temperature K	ΔH (J)	ΔS JK^{-1}	TΔS (J)	ΔG (J)
263	5614	20.5	5392	+ 227
273	6006	22.0	6006	0
283	6391	23.4	6622	–231

It is clear from the above table that ΔH is positive at all temperatures. ΔS is also positive because disorder increases from ice to water because water is more random state than ice. However, ΔG changes from +ve to –ve when temperature increases.

At 263K, ΔG is + ve indicating that the reaction is non-spontaneous or ice is more stable than water.

At 273K, ΔG = 0 indicating equilibrium between ice and water.

At 283K, ΔG becomes negative indicating that the conversion is spontaneous *i.e.,* water is a more stable state than ice.

Let us consider another example of manufacture of iron. Iron is obtained from its oxide ore, Fe_2O_3. Let us see, can we get iron simply by heating Fe_2O_3 as :

$$Fe_2O_3\ (s) \longrightarrow 2Fe\ (s) + \frac{3}{2} O_2\ (g)$$

The feasibility of this decomposition reaction can be predicted on the basis of $\Delta_r G^\circ$. It has been observed that at room temperature $\Delta_r H^\circ$ is +824.0 kJ mol^{-1} (unfavourable) and $\Delta_r S$ is 0.276 kJ K^{-1} mol^{-1} (favourable). However, $\Delta_r H^\circ$ has very large positive value and cannot be overweighed by –TΔS even at very high temperature. For example, at 298 K,

$$\Delta_r G^\circ = + 824.0 - 298\ (0.276) = + 742\ \text{kJ mol}^{-1}$$

Obviously, the large positive value of $\Delta_r H$ cannot be overweighed at any reasonable temperature. As we know that usual method of reducing Fe_2O_3 to iron is by use of reducing agent, carbon. The decomposition of Fe_2O_3 which is non-spontaneous is compensated by highly spontaneous process of combustion of carbon :

$$C\ (\text{graphite}) + O_2\ (g) \longrightarrow CO_2(g)$$

The overall reaction may be written as :

$$2\ Fe_2O_3\ (s) + 3\ C(s) \longrightarrow 4\ Fe\ (s) + 3\ CO_2\ (g)$$

The enthalpy change for this reaction, $\Delta_r H^\circ$ = + 467.9 kJ mol^{-1} and entropy change $\Delta_r S^\circ$ = +0.5603 kJ mol K^{-1}. However, the value of $-T\Delta_r S^\circ$ (– 167 kJ mol^{-1}) is not large enough to overcome the positive enthalpy change at 298 K. But, with increase in

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temperature, the contribution of $-T\Delta_r S^\circ$ will become more negative at higher temperature and will overtake the positive enthalpy change.

Let us calculate the temperature above which $\Delta_r G^\circ$ becomes negative so that the reaction becomes spontaneous. For this, let us first calculate the temperature, T at which $\Delta_r G^\circ$ is zero.

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

$$0 = +467.9 \text{ kJ mol}^{-1} - T\,(0.5603 \text{ kJ mol}^{-1} \text{ K}^{-1})$$

$$\text{or } T = \frac{467.9}{0.5603} = 835.1 \text{ K or } (562.1^\circ\text{C})$$

This means that the Gibbs energy change becomes 0 at 562.1°C and at higher temperature, it will be negative. Thus, for the reduction of Fe_2O_3 with carbon, temperature of the furnace in iron metallurgy must be kept higher than 562.1°C.

GIBBS ENERGY CHANGE AND NON-MECHANICAL WORK (USEFUL WORK)

In addition to predicting the spontaneity of a process, Gibbs energy change is also related to useful work (other than pressure-volume work) that can be obtained from the system. It can be shown that Gibbs energy change of a process is equal to the maximum possible work that can be derived from the process as given below.

From first law of thermodynamics, we know

$$\Delta U = q - w$$

where q is the heat absorbed by the system and w is the work done by the system. The work may be expansion work as well as non-expansion work. The non-expansion work can be used for useful effects; such as electrical work. This is called non pressure volume work or useful work. The work due to expansion at constant temperature, known as pressure-volume work is given by $p\Delta V$. Thus,

$$\Delta U = q - w_{\text{expansion}} - w_{\text{non-expansion}}$$

$$= q - p\Delta V - w_{\text{non-expansion}} \quad ...(i)$$

or $$q = \Delta U + p\Delta V + w_{\text{non-expansion}}$$

Now, $$\Delta U + p\Delta V = \Delta H$$

$\therefore$ $$q = \Delta H + w_{\text{non-expansion}} \quad ...(ii)$$

For a process carried out reversibly at constant temperature,

$$\Delta S = \frac{q_{rev}}{T}$$

or $$q_{rev} = T\Delta S$$

Substituting in eqn (*ii*)

$$T\Delta S = \Delta H + w_{\text{non-expansion}}$$

$$\Delta H - T\Delta S = -w_{\text{non-expansion}}$$

But $\Delta H - T\Delta S = \Delta G$ so that

$$\Delta G = -w_{\text{non-expansion}}$$

or $$-\Delta G = w_{\text{non-expansion}} = w_{\text{useful}}$$

But non-expansion work is regarded as useful work. Thus, the decrease in free energy of a system during a process is a measure of maximum useful work done during the change. Therefore, **Gibbs energy, G of a system is a measure of its capacity to do useful work.**

If the work involved is electrical work as in case of electrochemical cells, then ΔG is related to the electrical work done in the cell. If E is the e.m.f. of the cell and *n* mole of electrons are involved, then electrical work done will be

$-\Delta G = nFE$ or $\Delta G = -nFE$

where F is Faraday constant = 96500 C

If reactants and products are in the standard states, then

$$\Delta G^\circ = -nFE^\circ$$

where E° is standard e.m.f. of the cell.

SOLVED EXAMPLES

Example 59.

For the melting of ice at 25°C :

$$H_2O(s) \longrightarrow H_2O(l)$$

the enthalpy of fusion is 6.97 kJ mol^{-1} and entropy of fusion is 25.4 J mol^{-1} K^{-1}. Calculate the free energy change and predict whether melting of ice is spontaneous or not at this temperature. *(H.P.S.B. 2005)*

Solution : For the melting of ice at 25°C (or 298 K)

$\Delta H = 6.97$ kJ mol^{-1}

$\Delta S = 25.4$ J mol^{-1} K^{-1} $= 25.4 \times 10^{-3}$ kJ mol^{-1} K^{-1}

Now, $\Delta G = \Delta H - T\Delta S$

$\therefore$ $\Delta G = 6.97 - 298 \times 25.4 \times 10^{-3}$

$= 6.97 - 7.57 =$ **–0.6 kJ mol^{-1}.**

Since ΔG is negative, the melting of ice at 25°C is spontaneous.

Example 60.

Enthalpy and entropy changes of a reaction are 40.63 kJ mol^{-1} and 108.8 J K^{-1}mol^{-1} respectively. Predict the feasibility of the reaction at 27°C .

Solution : $\Delta H = 40.63$ kJ mol^{-1} $= 40630$ J K^{-1} mol^{-1}

$\Delta S = 108.8$ J K^{-1} mol^{-1}

$T = 27^\circ\text{C} = 27 + 273 = 300$ K

Now $\Delta G = \Delta H - T\Delta S$

$= 40630$ J mol^{-1} – (300 K) × (108.8 J K^{-1} mol^{-1})

$\Delta G =$ **7990 J mol^{-1}.**

Since ΔG is positive, the reaction is not feasible in the forward direction.

Example 61.

ΔH and ΔS for the reaction :

$$Ag_2O(s) \longrightarrow 2Ag(s) + \frac{1}{2} O_2(g)$$

are 30.56 kJ mol^{-1} and 66.0 J K^{-1} mol^{-1} respectively. Calculate the temperature at which the Gibbs energy change for the reaction will be zero. What will be the direction of the reaction at this temperature and at temperature below this temperature and why ? *(A.I.S.E. 2000)*

Solution. According to Gibbs Helmholtz equation,

$\Delta G = \Delta H - T\Delta S$

For, $\Delta G = 0$

$0 = \Delta H - T\Delta S$ or $\Delta H = T\Delta S$

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or $T = \frac{\Delta H}{\Delta S}$

Here, $\Delta H = 30.56$ kJ mol^{-1} = 30560 J mol^{-1}, $\Delta S = 6.6$ J K^{-1} mol^{-1}

$\therefore \quad T = \frac{30560}{6.6} = \mathbf{4630\ K.}$

(*i*) At 4630 K, the reaction will be at equilibrium because ΔG is zero.

(*ii*) Below this temperature, ΔG will be +ve because both ΔH and $T\Delta S$ are positive and $\Delta H > T\Delta S$ ($\Delta H - T\Delta S$ = +ve).

Therefore, the reaction will not be spontaneous below this temperature.

❑ Example 62.

Predict whether it is possible or not to reduce magnesium oxide using carbon at 298 K according to the reaction :

MgO (s) + C(s) ⟶ Mg(s) + CO (g)

$\Delta_r H^\circ$ = + 491.18 kJ mol^{-1} and $\Delta_r S^\circ$ = 197.67 JK^{-1} mol^{-1}

If not at what temperature, the reaction becomes spontaneous. **N.C.E.R.T.**

Solution : We know

$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$

$\Delta_r H^\circ = +491.18$ kJ mol^{-1},

$\Delta_r S^\circ = 197.67 \times 10^{-3}$ kJ mol^{-1} K^{-1}, T = 298 K

$\therefore \quad \Delta_r G^\circ = 491.18$ kJ mol^{-1} – 298 K × (197.67 × 10^{-3} kJ mol^{-1} K^{-1})

= 491.18 kJ mol^{-1} – 58.9 kJ mol^{-1}

= 432.28 kJ mol^{-1}

Since Gibbs energy change is positive, therefore, at 298 K, the reaction is not possible.

Let us calculate T at which $\Delta_r G^\circ$ becomes zero

$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = 0$

$\therefore \quad T = \frac{\Delta_r H}{\Delta_r S} = \frac{491.18\ \text{kJ mol}^{-1}}{197.67 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1}}$

= 2484.8 K

Therefore, the reaction will be spontaneous above 2484.8 K (or 2211.8°C).

Practice Problems

39. Calculate the entropy change involved in the vaporisation of water at 373 K to vapours at the same temperature (Latent heat of vaporisation = 2.275 kJ/g).

40. 30.4 kJ of heat is required to melt 1 mol of sodium chloride. The entropy change during melting is 28.4 J mol^{-1} K^{-1}. Calculate the melting point of sodium chloride.

41. Calculate entropy changes of fusion and vaporisation for chlorine from the following data :

$\Delta_{fus}H = 6.40$ kJ mol^{-1} m.p.= –102°C

$\Delta_{vap}H = 20.4$ kJ mol^{-1} b.p. = –34°C

42. $\Delta_{vap}S$ of acetone is 93.0 JK^{-1} mol^{-1}. If boiling point of acetone is 56°C, calculate the heat required for the vaporisation of 1 g of acetone.

43. The enthalpy of vaporisation of benzene (C_6H_6) is 30.8 kJ mol^{-1} at its boiling point (80.1°C). Calculate the entropy change in going from :

(*i*) liquid to vapour, and

(*ii*) vapour to liquid at 80.1°C.

44. $\Delta_{vap}H^\circ$ for water is 40.73 kJ mol^{-1} and $\Delta_{vap}S^\circ$ is 109 J K^{-1} mol^{-1}. Calculate the temperature at which liquid water will be in equilibrium with water vapour.

45. Calculate the entropy change of n-hexane when 1 mole of it evaporates at 341.7 K ($\Delta_{vap}H$ = 29.0 kJ mol^{-1}).

46. Calculate the Gibbs energy change on dissolving one mole of sodium chloride at 25°C.

Lattice energy = + 777.8 kJ mol^{-1}

Hydration of NaCl = – 774.1 kJ mol^{-1}

ΔS at 25°C = 43 JK^{-1} mol^{-1}

47. The values of ΔH and ΔS for two reactions are given below :

Reaction A : $\Delta H = -10.5 \times 10^3$ J mol^{-1}, $\Delta S = +31$ J K^{-1} mol^{-1}

Reaction B : $\Delta H = -11.7 \times 10^3$ J mol^{-1}, $\Delta S = -105$ J K^{-1} mol^{-1}

Decide whether these reactions are spontaneous or not at 298 K. *(Pb. S.B.E. 1993)*

48. At what temperature does the reduction of lead oxide to lead by carbon becomes spontaneous?

$PbO + C \longrightarrow Pb(s) + CO(g)$

For the reaction, ΔH and ΔS at 25°C are 108.4 kJ mol^{-1} and 190 JK^{-1} mol^{-1} respectively.

(A.I.S.E. 2001, H.P.S.B. 2005)

49. For the reaction at 298 K

$2A + B \longrightarrow C$

$\Delta H = 40$ kJ mol^{-1} and $\Delta S = 0.2$ kJ K^{-1} mol^{-1}

At what temperature will the reaction becomes spontaneous considering ΔH and ΔS to be constant over the temperature range. **N.C.E.R.T.**

Answers to Practice Problems

39. 109.78 JK^{-1} mol^{-1}

40. 1070.4 K

41. 37.4 JK^{-1} mol^{-1}, 85.3 JK^{-1} mol^{-1}.

42. 527.5 J

43. (*i*) 87.2 JK^{-1} mol^{-1} (*ii*) –87.2 JK^{-1} mol^{-1}

44. 373.67 K

45. 84.87 JK^{-1} mol^{-1}

46. $\Delta H = 777.8 - 774.1 = 3.7$ kJ mol^{-1}

$\Delta G = -9.11$ kJ mol^{-1}.

47. Reaction A : Spontaneous and Reaction B : Non-spontaneous.

48. Above 570.5 K.

49. 2000 K.

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STANDARD GIBBS ENERGY CHANGE

The **standard Gibbs energy change** is defined as **the Gibbs energy change for a process in which the reactants in their standard states are**

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converted to the products in their standard states.

It may be noted that like enthalpy, the Gibbs energy depends upon the states of reactants and products, the temperature and the pressure under which the reaction takes place. Therefore, it is convenient to fix ***a standard or a reference state*** for reporting data.

According to latest **thermodynamic convention, the standard state of a substance at a specified temperature is its pure form at 1 bar.** Standard state is represented by the superscript '°' and therefore ΔG° represents standard free energy change. For example standard state of hydrogen gas at 298 K is the pure gas at 1 bar pressure and standard state of liquid ethanol at 298 K is pure liquid ethanol at 298 K and 1 bar. Similarly standard state of solid aluminium oxide at 298 K is solid Al_2O_3 at 298 K and 1 bar specified pressure. It may be noted that physical state should be specified because we can speak of standard states of the solid, liquid or vapour phases of methanol which are the pure solid, the pure liquid or the pure vapour respectively at 1 bar pressure in each case.

Therefore, **the standard Gibbs energy change of a reaction is the Gibbs energy change when all the reactants and products are in their standard states.**

The standard Gibbs energy change of a reaction can be calculated from the standard Gibbs energy of formation of different substances in reactants and products.

The **standard Gibbs energy of formation of a substance** is defined **as the Gibbs energy change when one mole of the substance is formed from its elements in their standard states.** It is expressed as $\Delta_f G^\circ$

The standard Gibbs energies of formation of some common substances at 298 K are given in Table 12.

Like the standard enthalpy of formation of an element, **the standard Gibbs energy of formation of an element in its standard state is assumed to be zero.**

Thus, standard Gibbs energy change of a reaction is,

$$\Delta G = \Sigma \Delta_f G^\circ \text{ (products)} - \Sigma \Delta_f G^\circ \text{ (reactants)}$$

$$= \left[\begin{array}{c}\text{Sum of the standard Gibbs energy} \\ \text{of formation of products}\end{array}\right] - \left[\begin{array}{c}\text{Sum of the standard Gibbs energy of} \\ \text{formation of reactants}\end{array}\right]$$

Table 12. Standard Gibbs energies of formation of some substances.

Substance	$(\Delta_f G^\circ)$	Substance	$(\Delta_f G^\circ)$
Solid substances		**Gaseous substances**	
Al_2O_3	– 1582.4	Br_2	3.1
BaO	– 528.4	CH_4	– 50.79
$BaCO_3$	– 1139.0	C_2H_6	229.0
$BaSO_4$	– 1465.0	C_3H_8	270.0
CaO	– 604.2	C_4H_{10} (*n*–butane)	310.0
$CaCO_3$	– 1129.0	C_4H_{10} (iso–butane)	310.00
$Ca(OH)_2$	– 896.6	C_2H_2	209.2
CuO	– 127.0	C_2H_4	219.4
Fe_2O_3	– 741.0	C_3H_6	266.9
KCl	– 408.3	C_4H_8 (but–1–ene)	307.4
NaCl	– 384.0	C_4H_8 (cis–but–2–ene)	301.0
NH_4Cl	– 203.0	C_4H_8 (trans–but–2–ene)	297.0
P(white)	0.0	CO	– 137.3
P(red)	– 12.0	CO_2	– 394.4
PbO_2	– 219.0	Cl (*g*)	105.4
SiO_2	– 805.0	HCl	– 95.27
ZnO	– 318.2	H_2O	– 228.0
Liquid substances		H_2O_2	– 103.3
CH_3OH	– 166.2	H_2S	– 33.0
C_2H_5OH	– 174.8	N_2O	104.0
C_6H_6	– 124.5	NO	86.69
CH_3COOH	– 392.0	NO_2	51.84
H_2O	– 237.2	NH_3	– 16.6
H_2O_2	– 120.4	NO	86.7
HCl(*aq*)	– 131.3	O_3	163.4
H_2SO_4	– 690.0	SO_2	–300.4

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Note. It may be noted that the temperature is not a part of the definition of a standard state and it is not restricted to 25°C (or 298K). Therefore, it is possible to speak the standard state of a substance at 273K, 298K, 373 K or any other temperature. However, literature records most of the data at 25°C or 298.15K.

Earlier, the standard state of a substance was taken as its pure form under 1 atm pressure (101.325 kPa). Recently, IUPAC has recommended that standard pressure should be taken as 1 bar.

The older unit of measurement of pressure had been **atmosphere** and 1 atm is exactly equal to 101325 Nm^{-2} or 101.325 kPa.

SI unit of pressure is pascal (Pa) and 1Pa = $1Nm^{-2}$. Slightly different from 1 atm is the 1 bar which is exactly 10^5Pa (so that 1 atm = 1.01325 bar). Thus, 1 bar = 10^5 Pa and 1 atm = 101.325 kPa = 1.01325 bar.

Thus, bar has the advantage of being immediately converted to fundamental units without involving lengthy calculations. Therefore, 1 bar is taken as standard pressure.

SOLVED EXAMPLES

Example 63.

Calculate the standard Gibbs free energy change from the free energies of formation data for the following reaction :

$$C_6H_6(l) + \frac{15}{2} O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(g)$$

Given that $\Delta_f G^\circ [C_6H_6(l)] = 172.8\ kJ\ mol^{-1}$

$\Delta_f G^\circ [CO_2(g)] = -394.4\ kJ\ mol^{-1}$

$\Delta_f G^\circ [H_2O(g)] = -228.6\ kJ\ mol^{-1}$.

Solution : $\Delta G = \Sigma \Delta_f G^\circ$ (products) $- \Sigma \Delta_f G^\circ$ (reactants)

$= \{6\Delta_f G^\circ [CO_2(g)] + 3\Delta_f G^\circ [H_2O(g)]\}$

$- \{\Delta_f G^\circ [C_6H_6(l)] + \frac{15}{2} \Delta_f G^\circ [O_2(g)]\}$

$= \{(6 \times -394.4) + 3 \times (-228.6)\}$

$- \{172.8 + 0\} = \mathbf{-3225\ kJ\ mol^{-1}}$.

Example 64.

Consider the reaction :

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l)$$

$\Delta G^\circ = -1010.5\ kJ$

Calculate $\Delta_f G^\circ [NO(g)]$ *if* $\Delta_f G^\circ [NH_3(g)] = -16.6\ kJ\ mol^{-1}$ *and* $\Delta_f G^\circ [H_2O(l)] = -237.2\ kJ\ mol^{-1}$

Solution : For the reaction

$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6\ H_2O(l)$

$\Delta G^\circ = -1010.5\ kJ\ mol^{-1}$

$\Delta G^\circ = 4\Delta_f G^\circ [NO(g)] + 6\Delta_f G^\circ [H_2O(l)]$

$-\{4\Delta_f G^\circ [NH_3(g)] + 5\Delta_f G^\circ [O_2(g)]\}$

$\therefore \Delta G^\circ = -1010.5\ kJmol^{-1}$,

$\Delta_f G^\circ [H_2O(l)] = -237.2\ kJ\ mol^{-1}$,

$\Delta_f G^\circ [NH_3(g)] = -16.6\ kJ\ mol^{-1}$

and $\Delta_f G^\circ [O_2(g)] = 0$ (convention)

$\therefore -1010.5 = 4\Delta_f G^\circ [NO(g)] + 6 \times (-237.2)$

$- 4 \times (-16.6) - 5 \times 0$

$4\Delta_f G^\circ [NO(g)] = -1010.5 + 1423.2 - 66.4$

$= 346.3\ kJ\ mol^{-1}$

$\Delta_f G^\circ [NO(g)] = \mathbf{86.6.\ kJ\ mol^{-1}}$.

Example 65.

Calculate $\Delta_r G^\circ$ *for the following reactions using* $\Delta_f G^\circ$ *values and predict which reactions are spontaneous.*

(a) $Ca(s) + Cl_2(g) \longrightarrow CaCl_2(s)$

(b) $HgO(s) \longrightarrow Hg(l) + \frac{1}{2} O_2(g)$

(c) $NH_3(g) + 2O_2(g) \longrightarrow HNO_3(l) + H_2O(l)$

$\Delta_f G^\circ$ *values (kJ* mol^{-1}*) are :*

$CaCl_2(s) = -748.1$, $HgO(s) = -58.84$

$NH_3(g) = -16.45$, $HNO_3(l) = -80.71$,

$H_2O(l) = -237.13$

Solution : $\Delta_r G^\circ$ can be calculated by using the relation :

$\Delta_r G^\circ = \Sigma \Delta_f G^\circ$ (products) $- \Sigma \Delta_f G^\circ$ (reactants)

(a) $Ca(s) + Cl_2(g) \longrightarrow CaCl_2(s)$

$\Delta_r G^\circ = \Delta_f G^\circ [CaCl_2(s)] - \{\Delta_f G^\circ [Ca(s)] + \Delta_f G^\circ [Cl_2(g)]\}$

$= -748.1 - (0 + 0) = \mathbf{-748.1\ kJ}$.

Reaction is **spontaneous.**

(b) $HgO(s) \longrightarrow Hg(l) + \frac{1}{2} O_2(g)$

$\Delta_r G^\circ = \Delta_f G^\circ [Hg(l)] + \frac{1}{2} \Delta_f [O_2(g)] - \Delta_f G^\circ [HgO(s)]$

$= 0 + 0 - (-58.54) = \mathbf{58.84\ kJ}$.

Reaction is **not spontaneous.**

(c) $NH_3(g) + 2O_2(g) \longrightarrow HNO_3(l) + H_2O(l)$

$\Delta_r G^\circ = \Delta_f G^\circ [HNO_3(l)] + \Delta_f G^\circ [H_2O(l)] - \{\Delta_f G^\circ [NH_3(g)] + 2\Delta_f G^\circ [O_2(g)]\}$

$= -80.71 + (-237.13) - \{-16.45 + 0\}$

$= -80.71 - 237.13 + 16.45 = \mathbf{-301.39\ kJ}$.

Reaction is **spontaneous.**

Example 66.

Silane (SiH_4) *burns in air as :*

$SiH_4(g) + 2O_2(g) \longrightarrow SiO_2(s) + 2H_2O(l)$

The standard Gibbs energies of formation of $SiH_4(g)$, $SiO_2(s)$ *and* $H_2O(l)$ *are + 52.3, – 805.0 and – 228.6 kJ* mol^{-1} *respectively. Calculate Gibbs energy change for the reaction and predict whether the reaction is spontaneous or not.* **N.C.E.R.T.**

Solution : $SiH_4(g) + 2O_2(g) \longrightarrow SiO_2(g) + 2H_2O(l)$

$\Delta_r G^\circ = \Delta_f G^\circ (SiO_2) + 2\Delta_f G^\circ (H_2O) - [\Delta_f G^\circ (SiH_4) + 2\Delta_f G^\circ (O_2)]$

$= -805.0 + 2(-228.6) - [+52.3 + 2(0)]$

$= -805.0 - 457.2 - 52.3$

$= \mathbf{-1314.5\ kJ}$.

Since $\Delta_r G^\circ$ is negative, the reaction will be **spontaneous.**

Example 67.

In a fuel cell methanol is oxidised with oxygen as :

$$CH_3OH(l) + \frac{3}{2} O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

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Calculate the standard Gibbs energy change for the reaction that can be converted into electrical work. If standard enthalpy of combustion for methanol is –726 kJ mol^{-1}, calculate the efficiency of conversion of Gibbs energy into useful work. The standard Gibbs energies of formation, $\Delta_f G°$ (kJ mol^{-1}) are :
CO_2 (g) = – 394.4, H_2O (l) = – 237.2,
CH_3OH (l) = – 166.2 **N.C.E.R.T.**

Solution : For the reaction :

$$CH_3OH\,(l) + \frac{3}{2}\,O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(l)$$

$$\Delta_r G° = \Delta_f G°\,(CO_2) + 2\Delta_f G°\,(H_2O) - \{\Delta_f G°\,(CH_3OH) + \frac{3}{2}\Delta_f G°\,(O_2)\}$$

$$= -394.4 + 2(-237.2) - (-166.2) - 0$$

$$= -394.4 - 474.4 + 166.2$$

$$= -702.6 \text{ kJ mol}^{-1}$$

∴ Gibbs energy change which can be converted to electrical work = 702.6 kJ mol^{-1}

$$\text{Now, efficiency} = \frac{\Delta G}{\Delta H}$$

$$= \frac{702.6}{726.0} \times 100 = \mathbf{96.78\%}$$

Practice Problems

50. Consider the reaction :

$$2NO(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

Calculate the standard Gibbs energy change at 298 K and predict whether the reaction is spontaneous or not. $\Delta_f G°$ (NO) = 86.69 kJ mol^{-1}, $\Delta_f G°$ (NO_2) = 51.84 kJ mol^{-1}.

51. Calculate $\Delta_r G°$ for the reaction :

$$C_6H_{12}O_6(s) + 6O_2\,(g) \longrightarrow 6\,CO_2\,(g) + 6H_2O\,(l)$$

$\Delta_f G°$ values (kJ mol^{-1}) are :

$C_{12}H_{12}O_6(s)$ = –910.2, CO_2 (g) = – 394.4,
H_2O (l) = –237.2

Answers to Practice Problems

50. –69.7 kJ, spontaneous reaction.

51. –2879.4 kJ.

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GIBBS ENERGY CHANGE AND EQUILIBRIUM CONSTANT

So far we have considered free energy changes in irreversible reactions. However, as we have learnt, 'reversible' under strict thermodynamic sense is a special case of carrying out a process such that system at all times is in perfect equilibrium with its surroundings. For a chemical reaction, the term reversible means that a given reaction, can proceed in either direction simultaneously so that a dynamic equilibrium is set up.

This means that the reaction should proceed with a decrease in free energy in both the directions. However this is not possible. Therefore, we say that at equilibrium total free energy of the system is minimum. If it is not minimum, the system would spontaneously change to configuration of lower free energy.

Free energy is an extensive property and therefore, its value for a given substance will depend on the concentration of the substance. Let us consider a general reaction :

$$A + B \rightleftharpoons C + D$$

The Gibbs energy of reaction, $\Delta_r G$ is related to the composition of the reaction mixture and the standard reaction Gibbs energy, $\Delta_r G°$ as :

$$\Delta_r G = \Delta_r G° + RT \ln Q \qquad ...(vii)$$

where,

$\Delta_r G$ is the reaction Gibbs energy change at a definite, fixed composition of the mixture.

$\Delta_r G°$ is the difference in standard Gibbs energies of formation of the products and the reactants both in their standard states

Q is the reaction quotient and

R is the gas constant having the value 8.314 J K^{-1} mol^{-1}.

If the species are gases, these concentrations are expressed in partial pressures and the reaction quotient will be Q_p and if the species are in solution, the reaction quotient will be expressed in terms of molar concentrations as Q_c.

At equilibrium Q = K, called equilibrium constant and $\Delta_r G$ = 0 because the reaction mixture has no tendency to change in either direction. Therefore, the above equation becomes :

$$0 = \Delta_r G° + RT \ln K$$

$$\text{or} \quad \Delta_r G° = -RT \ln K$$

$$\text{or} \quad \Delta_r G° = -2.303\,RT \log K \qquad ...(i)$$

The above equation may also be written as :

$$K = e^{-\Delta_r G°/RT}$$

$$\text{or} \quad = 10^{-\Delta_r G°/2.303RT}$$

This equation is very important in chemical thermodynamics because it gives relation between equilibrium constant for any process (physical or chemical) and standard Gibbs energy change. We can also conclude :

$K < 1$ when $\Delta_r G° > 0$

$K > 1$ when $\Delta_r G° < 0$

We also know that

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° = -RT \ln K \qquad ...(ii)$$

This also means that the equilibrium constant is related to $\Delta_r H°$ and $\Delta_r S°$.

Rearranging the above equation

$$RT \ln K = T\Delta_r S° - \Delta_r H°$$

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or $$\ln K = \frac{T\Delta_r S^\circ - \Delta_r H^\circ}{RT} \quad ...(iii)$$

For strongly **endothermic reactions,** $\Delta_r H^\circ$ may be large and positive. In such case, value of K will be much smaller than 1. This means that the reaction is unlikely to form much products.

In case of **exothermic reactions,** $\Delta_r H^\circ$ is large and negative and $\Delta_r G^\circ$ is also large and negative. In such cases, K will be larger than 1. Therefore, we generally expect strong exothermic reactions to have large K and hence these go to near completion.

Now $\Delta_r G^\circ$ also depends upon $\Delta_r S^\circ$ and therefore, changes in entropy may also be considered. These changes will also affect the value of K or extent of a chemical reaction depending upon whether $\Delta_r S^\circ$ is positive or negative using eqn. (*vii*)

(*i*) It is possible to have an estimate of ΔG° from the measurement of ΔH° and ΔS° and then calculate K at any temperature for economic yields of the products.

(*ii*) If K is measured directly in the laboratory, value of ΔG° at any other temperature can be calculated.

SOLVED EXAMPLES

❑ Example 68.

For the water gas reaction

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

the standard Gibbs energy for the reaction at 1000 K is –8.1 kJ mol^{-1}. Calculate its equilibrium constant. **N.C.E.R.T.**

Solution : We know

$$\Delta_r G^\circ = -2.303\ RT \log K$$

or $$\log K = \frac{-\Delta_r G}{2.303\ RT}$$

$\Delta_r G^\circ = -8.1$ kJ mol^{-1}, T = 1000 K,

$R = 8.314 \times 10^{-3}$ kJ mol^{-1} K^{-1}

$$\therefore \quad \log K = -\frac{-8.1}{2.303 \times 8.314 \times 10^{-3} \times 1000}$$

$$= 0.423$$

or $K = \mathbf{2.64.}$

❑ Example 69.

Calculate $\Delta_r G^\circ$ for conversion of oxyen to ozone :

$$\frac{3}{2} O_2(g) \longrightarrow O_3(g) \text{ at 298 K.}$$

K_p for this conversion is 2.47×10^{-29} **N.C.E.R.T.**

Solution : We know

$$\Delta_r G^\circ = -2.303\ RT \log K$$

R = 8.314 J mol^{-1} K^{-1}, T = 298 K, K = 2.47×10^{-29}

$\therefore \Delta_r G^\circ = -2.303 \times (8.314\ J\ mol^{-1}\ K^{-1}) \times (298\ K) \times \log (2.47 \times 10^{-29})$

$= \mathbf{163.2\ kJ\ mol^{-1}.}$

❑ Example 70.

Calculate equilibrium constant for the reaction at 400 K.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

$\Delta H^\circ = 77.2\ kJ\ mol^{-1}$ and

$\Delta S^\circ = 122\ JK^{-1}\ mol^{-1}$ at 400 K. *(Pb.S.B. 2005)*

Solution : $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta H^\circ = 77200$ J mol^{-1},

$\Delta S^\circ = 122$ JK^{-1} mol^{-1}, T = 400 K

$\Delta G^\circ = 77200 - 400 \times 122$

$= 77200 - 48800$

$= 28400$ JK^{-1} mol^{-1}

Now, $\Delta G^\circ = -RT \ln K$

$= -2.303\ RT \log K$

$28400 = -2.303 \times 8.314 \times 400 \log K$

or $$\log K = -\frac{28400}{2.303 \times 8.314 \times 400} = -3.708$$

or $\log K = -\bar{4}.292$

$K = \text{Antilog } (\bar{4}.292) = \mathbf{1.96 \times 10^{-4}.}$

❑ Example 71.

The standard Gibbs energies ($\Delta_f G^\circ$) for the formation of SO_2 (g) and SO_3(g) are – 300.0 and –371.0 kJ mol^{-1} at 300 K respectively.

Calculate ΔG and equilibrium constant for the following reaction at 300 K :

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Solution : $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$\Delta_r G^\circ = 2\ \Delta_f G^\circ(SO_3) - 2\Delta_f G^\circ(SO_2) - \Delta_f G^\circ(O_2)$

$= 2(-371) - 2(-300) - 0$

$= -742 + 600 = -142$ kJ mol^{-1}

Now $$\log K = -\frac{\Delta_r G^\circ}{2.303\ RT}$$

$\Delta_r G^\circ = -142$ kJ mol^{-1}, R = 8.314×10^{-3} kJ mol^{-1}K^{-1}, T = 300 K

$$\log K = -\frac{-142}{2.303 \times 8.314 \times 10^{-3} \times 300}$$

$$= 24.72$$

$\therefore \quad K = \text{Antilog } (24.72)$

$= \mathbf{5.248 \times 10^{24}.}$

❑ Example 72.

At 60°C, dinitrogen tetroxide is 50% dissociated. Calculate the standard free energy change at this temperature and at one atmosphere **N.C.E.R.T.**

Solution: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Since N_2O_4 is 50% dissociated, then moles of N_2O_4 left and NO_2 formed are :

Moles of N_2O_4 left = 1–0.5 = 0.5

Moles of NO_2 formed = 2 × 0.5 = 1.0

Mole fraction of N_2O_4, $x_{NO_2} = \frac{0.5}{0.5 + 1.0} = \frac{0.5}{1.5}$

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Mole fraction of NO_2, $x_{NO_2} = \frac{1}{0.5+1.0} = \frac{1}{1.5}$

$$p_{N_2O_4} = x_{N_2O_4} \times p = \frac{0.5}{1.5} \times 1 = \frac{0.5}{1.5}$$

$$p_{NO_2} = x_{NO_2} \times p = \frac{1.0}{1.5} \times 1 = \frac{1.0}{1.5}$$

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{\left(\frac{1.0}{1.5}\right)^2}{\left(\frac{0.5}{1.5}\right)} = 1.33$$

$\Delta G^\circ = -2.303\ RT\ \log K_p$
$= -2.303 \times 8.314 \times 333 \times \log 1.33$
$= -2.303 \times 8.314 \times 333 \times 0.1239$
$= -790.0\ kJ\ mol^{-1}$

❑ Example 73.

Find out the value of equilibrium constant for the following reaction at 298 K

$2NH_3(g) + CO_2(g) \rightleftharpoons NH_2CONH_2(aq) + H_2O(l)$

Standard Gibbs energy change, $\Delta_f G^\circ$ at this temperature is –13.6 kJ mol^{-1}. **N.C.E.R.T.**

Solution: $\log K = -\frac{\Delta G^\circ}{2.303RT}$

$\Delta G^\circ = -13.6\ kJ\ mol^{-1}$, $R = 8.314\ JK^{-1}\ mol^{-1}$,
$T = 298\ K$

$$\log K = -\frac{-13.6 \times 10^3}{2.303 \times 8.314 \times 298}$$

$\log K = 2.38$

$\therefore\ K = \mathbf{2.40 \times 10^2}$

❑ Example 74.

It is planned to carry out the reaction :

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

at 1273 K and 1 bar pressure.

$\Delta_r H^\circ = 176\ kJ\ mol^{-1}$ *and* $\Delta_r S^\circ = 157.2\ kJ\ mol^{-1}$

(a) Is the reaction spontaneous at this temperature and pressure ?

(b) Calculate the value of K_p at 1273 K for the reaction.

Solution : (a) $\Delta_r G^\circ$ for the reaction at 1273 K

$\Delta_r G^\circ = \Delta_r H^\circ - T\,\Delta_r S^\circ$

$\Delta_r H^\circ = 176\ kJ\ mol^{-1}$, $\Delta_r S^\circ = 157.2\ J\ mol^{-1}$ and $T = 1273\ K$

$\therefore\ \Delta_r G^\circ = 176\ kJ\ mol^{-1} - 1273 \times 157.2 \times 10^{-3}\ kJ\ mol^{-1}$
$= 176 - 200.1$
$= -24.10\ kJ$

Since $\Delta_r G^\circ$ is negative, the reaction is spontaneous.

(b) (i) $\Delta_r G^\circ = -2.303\ RT \log K_p$

$$\text{or } \log K_p = -\frac{\Delta_r G^\circ}{2.303\ RT}$$

$\Delta_r G^\circ = -24.10\ kJ\ mol^{-1}$, $R = 8.314 \times 10^{-3}\ kJ\ mol^{-1}$, $T = 1273\ K$

$$\therefore \log K_p = -\frac{-24.10}{2.303 \times 8.314 \times 10^{-3} \times 1273}$$

$= 0.9887$

$\therefore\ K_p$ = Antilog (0.9887)

$= \mathbf{9.74.}$

❑ Example 75.

For the reaction at 298K

$2A(g) + B(g) \longrightarrow 2D(g)$

$\Delta U^\circ = -10.5\ kJ$ *and* $\Delta S^\circ = -44.1\ JK^{-1}$

Calculate ΔG° for the reaction and predict whether the reaction may occur spontaneous or not.

Solution : $\Delta H^\circ = \Delta U^\circ + \Delta n_g RT$

$\Delta U^\circ = -10.5\ kJ\ mol^{-1}$, $R = 8.314\ JK^{-1}mol^{-1}$, $T = 298\ K$

$\Delta n_g = 2 - (2 + 1) = -1$

$\therefore\ \Delta H^\circ = -10.5 - (1) \times 8.314 \times 10^{-3} \times 298$
$= -10.5 - 2.48$
$= -12.98\ kJ\ mol^{-1}$

Now $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
$= -12.98 - 298 \times (-44.1 \times 10^{-3})$
$= -12.98 + 13.14$
$= \mathbf{0.16\ kJ\ mol^{-1}}$

Since ΔG° is positive, the reaction is not spontaneous.

❑ Example 76.

Using the following data, calculate the value of equilibrium constant for the following reaction at 298 K.

$$\underset{\text{Acetylene}}{3HC \equiv CH} \rightleftharpoons \underset{\text{Benzene}}{C_6H_6(g)}$$

Assuming ideal behaviour

$\Delta_f G^\circ(HC \equiv CH) = 2.09 \times 10^5\ J\ mol^{-1}$
$\Delta_f G^\circ(C_6H_6) = 1.24 \times 10^5\ J\ mol^{-1}$,
$R = 8.314\ JK^{-1}\ mol^{-1}$

Can the reaction be recommended for the synthesis of benzene ?

Solution : ΔG° for the reaction :

$\Delta G^\circ = \Delta_f G^\circ(C_6H_6) - 3\,[\Delta_f G^\circ(HC \equiv CH)]$
$= 1.24 \times 10^5 - 3 \times 2.09 \times 10^5$
$= -5.03 \times 10^5$

Now, $\Delta G^\circ = -2.303\ RT \log K$

or $\log K = -\frac{\Delta G}{2.303\ RT} = 88.155$

$$= -\frac{-5.03 \times 10^5}{2.303 \times 8.314 \times 298} = 88.155$$

$\therefore\ K$ = Antilog (88.155)
$= \mathbf{1.43 \times 10^{88}}$

Since value of ΔG is negative, the reaction is feasible and may be recommended for making benzene.

Practice Problems

52. Calculate ΔG° for the reaction

$$NO(g) \rightleftharpoons \frac{1}{2} N_2(g) + \frac{1}{2} O_2(g)$$

if $K = 1.55 \times 10^{15}$ at 298 K.

53. The equilibrium constant for the reaction :

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

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is 73 at 25°C. Calculate standard free energy change.

54. Calculate the equilibrium constant for the following reaction at 298 K :

$$2H_2O\,(l) \longrightarrow 2H_2\,(g) + O_2\,(g)$$

$\Delta_f G°\,(H_2O) = -237.2$ kJ mol^{-1}, R = 8.314 J mol^{-1} K^{-1}.

55. The equilibrium constant for the reaction :

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COO\,C_2H_5(l) + H_2O(l)$$

has been found to be equal to 4 at 25°C. Calculate the free energy change for the reaction.

56. Calculate the entropy change for a reaction :

$$X \longrightarrow Y$$

Given that $\Delta H° = 28.40$ kJ mol^{-1} and equilibrium constant is 1.8×10^{-7} at 298 K.

57. Calculate the equilibrium constant for the following reaction at 298 K and 1 atmospheric pressure :

$$C\ (\text{graphite}) + H_2O(l) \longrightarrow CO(g) + H_2(g)$$

Given $\Delta_f H°$ at 298 K for $H_2O(l)$ = –286.0 kJ mol^{-1}

for $CO(g)$ = –110.5 kJ mol^{-1}

$\Delta S°$ at 298K for the reaction = 252.6 JK^{-1} mol^{-1}

(Pb. S.B.E. 2005)

58. For the equilibrium reaction :

$$2H_2\,(g) + O_2(g) \rightleftharpoons 2H_2O(l) \text{ at 298 K,}$$

$\Delta G° = -474.78$ kJ mol^{-1}. Calculate log K for it. (R = 8.314 J K^{-1} mol^{-1}). *(D.S.B. 2001)*

59. Calculate the equilibrium constant for the reaction :

$$NO\,(g) + \frac{1}{2}\,O_2\,(g) \rightleftharpoons NO_2\,(g)$$

Given ; $\Delta_f H°$ at 298 K : NO (g) = 90.4 kJ mol^{-1}, $NO_2(g)$ = 33.8 kJ mol^{-1} and $\Delta S°$ at 298 K = –70.8 JK^{-1} mol^{-1}.

60. $\Delta H°$ and $\Delta S°$ for the reaction :

$$Br_2\,(l) + Cl_2\,(g) \rightleftharpoons 2BrCl\,(g)$$

at 298K are 29.3 kJ mol^{-1} and 104.1 JK^{-1}mol^{-1} respectively. Calculate equilibrium constant for the reaction. *(Pb. S. B. 2004)*

Answers to Practice Problems

52. –86.7 kJ mol^{-1} **53.** –10.63 kJ mol^{-1}.
54. 7.19×10^{-84}. **55.** –3.434 kJ mol^{-1}.
56. –33.8 J mol^{-1} K^{-1}. **57.** 2.72×10^{-18}.
58. 83.21. **59.** 1.67×10^{6}.
60. 2.003.

Hints & Solutions on page 78

ABSOLUTE ENTROPIES AND THIRD LAW OF THERMODYNAMICS

Molecules of a substance may move in a straight line in any direction. They may spin like a top and the bonds in the molecules may stretch and compress. The motions of molecules are called translational, rotational and vibrational motion. When temperature of the system rises, the motion of molecules becomes more vigorous and entropy increases. On the other hand, when temperature is lowered, the entropy decreases.

The third law of thermodynamics deals with the entropies of the perfect crystalline substances at absolute zero of temperature. According to third law of thermodynamics :

at absolute zero the entropy of a perfectly crystalline substance is taken as zero.

This law was first formulated by German chemist Walther Nernst in 1906. Since entropy is related to disorder, therefore according to third law, at absolute zero, there is least disorder *i.e.* there is perfect order and, therefore, the entropy at perfect order is taken as zero. It may be noted that this law is true only for those substances which exist in the perfectly crystalline form at 0 K. However, if there are imperfections of any type in the perfect crystalline arrangement at 0 K, then the entropy will be larger than zero.

It may be **noted** that the statement of third law of thermodynamics is confined mainly to pure crystalline solids because theoretical arguments and practical evidences have shown that entropy of solutions and supercooled liquids is not zero at absolute zero (0 K).

Utility of Third Law of Thermodynamics

The third law of thermodynamics helps to calculate the absolute entropies of pure substances at different temperatures. The entropy (S) of the substance at different temperature T may be calculated by the measurement of heat capacity changes. If S_0 be the entropy of the substance at 0 K and S be its entropy at T K, then

$$\Delta S = S - S_0 = \int_0^T \frac{C_p}{T} dT$$

Since $S_0 = 0$, according to third law

$$S = \int_0^T \frac{C_p}{T} dT$$

The value of integral can be calculated from the graph of C_p/T against temperature (T). The area under the curve between 0 K and T K gives the value of integral and, thus, the value of S at temperature T.

When the entropy of one mole of the substance is expressed at standard state, *it is* called **standard molar entropy** of the substance and is denoted as S_m°. The standard entropies of various substances are given in Table 13. The standard entropy change ($\Delta_r S°$) for a chemical reaction is the difference in molar entropy between the products and the reactants in their standard states. It may be expressed as :

$$\Delta_r S° = \begin{bmatrix}\text{Sum of the standard}\\ \text{entropies of products}\end{bmatrix} - \begin{bmatrix}\text{Sum of the standard}\\ \text{entropies of reactants}\end{bmatrix}$$

or $\Delta_r S° = \Sigma S°\,(\text{products}) - \Sigma S°\,(\text{reactants})$

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or $\Delta_r S^\circ = \Sigma v_p S_m^\circ$ (products) $- \Sigma v_r S_m^\circ$ (reactants)

where v_p and v_r are stoichiometric coefficients for products and reactants.

For example, in a general reaction :

$aA + bB \longrightarrow cC + dD$

$$\Delta_r S_m^\circ = [cS_m^\circ(C) + d\,S_m^\circ(D)] - [a\,S_m^\circ(A) + b\,S_m^\circ(B)]$$

Table 13. Standard molar entropies of substances at 298 K. S_m° (J K^{-1} mol^{-1}).

Substance	Entropy
Solids	
Al	96.2
C(graphite)	5.7
C (diamond)	2.4
Cu	33.1
CaO	39.8
$CaCO_3$ (calcite)	92.9
$C_{12}H_{22}O_{11}$	360.8
$CuSO_4.5H_2O$	300.4
Fe	27.3
I_2	116.7
NaCl	72.1
Pb	64.8
Liquids	
Br_2	152.3
C_6H_6	173.3
C_2H_5OH	160.7
CH_3COOH	159.8
H_2O	69.9
Hg	76.0
Gases	
CO_2	213.7
CO	197.6
Cl_2	203.3
CH_4	186.2
H_2	130.7
He	126.2
H_2O	188.7
HCl	186.7
HBr	198.5
HI	206.3
N_2	191.6
NO_2	240.1
N_2O_4	304.3
NH_3	192.3
O_2	205.1
SO_2	248.5

SOLVED EXAMPLES

Example 77.

Calculate $\Delta_r S_m^\circ$ for the reaction :

$4Fe\,(s) + 3O_2\,(g) \longrightarrow 2Fe_2O_3\,(s)$

given that $S_m^\circ(Fe) = 27.3\ JK^{-1}mol^{-1}$, $S_m^\circ(O_2) = 205.0\ JK^{-1}\ mol^{-1}$ and $S_m^\circ(Fe_2O_3) = 87.4\ JK^{-1}\ mol^{-1}$.

Solution : For the reaction :

$4Fe\,(s) + 3O_2\,(g \longrightarrow 2\,Fe_2O_3\,(s)$

$\Delta_r S_m^\circ = 2\,S_m^\circ(Fe_2O_3) - [4 \times S_m^\circ(Fe) + 3 \times S_m^\circ(O_2)]$

$= 2 \times 87.4 - [4 \times 27.3 + 3 \times 205.0]$

$= \mathbf{-549.4\ J\ K^{-1}\ mol^{-1}}$

Example 78.

Calculate the entropy changes for the following reactions :

(i) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$

(ii) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

Entropies of different compounds are :

$CO(g) = 197.6\ JK^{-1}\ mol^{-1}$, $O_2(g) = 205.03\ JK^{-1}\ mol^{-1}$

$CO_2(g) = 213.6\ JK^{-1}\ mol^{-1}$, $H_2(g) = 130.6\ JK^{-1}\ mol^{-1}$

$H_2O(l) = 69.96\ JK^{-1}\ mol^{-1}$.

Solution : (*i*) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$

$\Delta S^\circ = \Sigma S^\circ$ (products) $- \Sigma S^\circ$(reactants)

$= 2S^\circ[CO_2(g)] - \{2S^\circ[CO(g)] + S^\circ[O_2(g)]\}$

$= 2(213.6) - \{2(197.6) + (205.03)\}$

$= 427.2 - 600.23$

$= -173.03\ JK^{-1}\ mol^{-1}$

(*ii*) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

$\Delta S^\circ = \{2S^\circ[H_2O(l)]\} - \{2S^\circ[H_2(g)] + S^\circ[O_2(g)]\}$

$= 2(69.96) - \{2(130.6) + 205.03\}$

$= 139.92 - 466.23$

$= \mathbf{-326.31\ JK^{-1}\ mol^{-1}}$

Example 79.

Calculate the standard molar entropy change for the formation of gaseous propane (C_3H_8) at 298 K.

$3C\ (graphite) + 4H_2\ (g) \longrightarrow C_3H_8\ (g)$

Standard molar entropies $S_m^\circ(JK^{-1}\ mol^{-1})$ are :

C (graphite) = 5.7, H_2 (g) = 130.7, C_3H_8 (g) = 270.2

Solution : Standard molar entropy change,

$\Delta_r S_m^\circ = S_m^\circ(C_3H_8) - [3\,S_m^\circ(C) + 4\,S_m^\circ(H_2)]$

$= 270.2 - [3 \times 5.7 + 4 \times 130.7]$

$= 270.2 - 539.9$

$= \mathbf{-269.7\ JK^{-1}\ mol^{-1}}$

Example 80.

Calculate the free energy change at 298 K for the reaction :

$Br_2(l) + Cl_2(g) \longrightarrow 2BrCl(g)$

$\Delta H = 29.3\ kJ$ at 298 K. The entropies of $Br_2(l)$, $Cl_2(g)$ and $BrCl(g)$ at the above temperature are 152.3, 223.0 and 239.7 J mol^{-1} K^{-1} respectively.

Solution : For the reaction,

$\Delta S = S(products) - S(reactants)$

$= 2 \times S(BrCl) - [S(Br_2) + S(Cl_2)]$

$= 2 \times 239.7 - [152.3 + 223.0]$

$= 479.4 - 375.3$

$= 104.1\ J$

Now, $\Delta G = \Delta H - T\Delta S$

$\Delta H = 29.3\ kJ = 29300\ J$, $T = 298\ K$

$\therefore$ $\Delta G = 29300 - (298 \times 104.1)$

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$= 29300 - 31021.8$

$= -$ **1721.8 J**

Since ΔG has negative value, the reaction is feasible at 298 K.

❑ **Example 81.**

Calculate the standard Gibbs energy change for the combustion of α-D glucose at 298 K:

$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$

Given that standard enthalpies of formation (kJ mol^{-1})

$C_6H_{12}O_6 = -1274.5$, $CO_2 = -393.5$, $H_2O = -285.8$.

Entropies (J K mol^{-1})

$C_6H_{12}O_6 = 212.1$, $O_2 = 205.0$, $CO_2 = 213.6$, $H_2O = 69.9$

Solution : $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta H^\circ = [6\Delta_f H^\circ(CO_2) + 6\Delta_f H^\circ(H_2O)] - [\Delta_f H^\circ(C_6H_{12}O_6) + 6\Delta_f H^\circ(O_2)]$

$= [6 \times (-393.5) + 6 \times (-285.8)] - [(-1274.5) + 6 \times 0]$ $[\because \Delta_f H^\circ(O_2) = 0]$

$= -2361.0 - 1714.8 + 1274.5 = -2801.3$ kJ mol^{-1}

$\Delta S^\circ = [6S^\circ(CO_2) + 6S^\circ(H_2O)] - [S^\circ(C_6H_{12}O_6) + 6^\circ(O_2)]$

$= [6 \times (213.6) + 6 \times (69.9)] - [(212.1) + 6 \times (205.0)]$

$= [1281.6 + 419.4] - [212.1 + 1230]$

$= 258.9$ JK^{-1} mol^{-1}

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta H^\circ = -2801.3$ kJ $= 2801300$ J mol^{-1}, $\Delta S^\circ = 258.9$, $T = 298$ K

$\therefore \Delta G^\circ = -2801300 - 298 \times (258.9)$

$= -2878452$ or $=$ **-2878.4 kJ mol^{-1}**

❑ **Example 82.**

Calculate the standard free energy change for the formation of methane at 298 K :

C (graphite) + $2H_2(g) \longrightarrow CH_4(g)$

The following data are given :

$\Delta_f H^\circ$(kJ mol^{-1}) : $CH_4(g) = -74.81$

S_m° (kJ mol^{-1}) : C (graphite) $= 5.70$, $H_2(g) = 130.7$

$CH_4(g) = 186.3$

Solution : $\Delta_r G^\circ$ can be calculated from the relation :

$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$

C (graphite) + $2H_2(g) \longrightarrow CH_4(g)$

$\Delta_r H^\circ = \Delta_f H^\circ(CH_4) - [\Delta_f H^\circ(C) + 2\Delta_f H^\circ(H_2)]$

$= -74.81 - 0 - 0 = -74.81$ kJ mol^{-1}

$\Delta_r S^\circ = S_m^\circ(CH_4) - [S_m^\circ(C) + 2S_m^\circ(H_2)]$

$= 186.3 - [5.70 + 2 \times 130.7]$

$= 186.3 - 267.1$

$= -80.8$ J K^{-1} mol^{-1}

$\therefore \Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$

$= -74.81 - 298 \times (-80.8 \times 10^{-3})$

$= -74.81 + 24.08 =$ **-50.73 kJ mol^{-1}**

❑ **Example 83.**

Calculate the standard Gibbs energy change for the formation of propane at 298 K :

$3C$ (graphite) + $4H_2(g) \longrightarrow C_3H_8(g)$

$\Delta_f H^\circ$ for propane, $C_3H_8(g) = -103.8$ kJ mol^{-1}

Given : $S_m^\circ[C_3H_8(g)] = 270.2$ JK^{-1} mol^{-1}

S_m°(graphite) $= 5.70$ JK^{-1} mol^{-1}

and $S_m^\circ[H_2(g)] = 130.7$ JK^{-1} mol^{-1}

(D.S.B. 2004, A.I.S.B. 2004)

Solution : $3C$ (graphite) + $4H_2(g) \longrightarrow C_3H_8(g)$

$\Delta_r H^\circ = \Delta_f H^\circ(C_3H_8) - \{3\Delta_f H^\circ(C) + 4\Delta_f H^\circ(H_2)\}$

$= -103.8 - 0 - 0 = -103.8$ kJ mol^{-1}

$\Delta_r S^\circ = S_m^\circ(C_3H_8) - \{3S_m^\circ(C) + 4S_m^\circ(H_2)\}$

$= 270.2 - \{3 \times 5.70 + 4 \times 130.7\}$

$= 270.2 - 539.9$

$= -269.7$ JK^{-1}

$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$

$= -103.8 - 298 \times (-269.7 \times 10^{-3})$

$=$ **-23.43 kJ**

Practice Problems

61. Calculate the standard free energy change for the reaction :

$H_2(g) + I_2(g) \longrightarrow 2HI(g)$ $\quad \Delta H^\circ = 51.9$ kJ mol^{-1}

Given : $S^\circ(H_2) = 130.6$ JK^{-1} mol^{-1},

$S^\circ(I_2) = 116.7$ JK^{-1}mol^{-1} and $S^\circ(HI) = 206.3$ JK^{-1}mol^{-1}.

62. Calculate $\Delta_r G^\circ$ for the reaction :

$CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$ $\Delta H^\circ = -282.8$ kJ

Standard entropies : $CO_2(g) = 213.6$, $CO(g) = 197.6$ and $O_2(g) = 205.0$ (all in J mol^{-1}). Predict whether the reaction is spontaneous or not at standard state.

63. Calculate the change of entropy, $\Delta_r S^\circ$ at 298 K for the reaction in which urea is formed from NH_3 and CO_2

$2NH_3(g) + CO_2(g) \longrightarrow NH_2CONH_2(aq) + H_2O(l)$

The standard entropies (JK^{-1} mol^{-1}) are :

$NH_2CONH_2(aq) = 174.0$, $H_2O(l) = 69.9$

$NH_3(g) = 192.3$, $CO_2(g) = 213.7$

64. Calculate the standard molar entropy change for the following reactions at 298 K :

(*a*) $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$

[$S^\circ(Fe_2O_3) = 87.4$, $S^\circ(Fe) = 27.3$, $S^\circ(O_2) = 205.1$ (all in JK^{-1} mol^{-1})]

(*b*) $Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$

[S° $Ca(OH)_2 = -74.5$, $S^\circ(Ca) = 41.42$, $S^\circ(H_2) = 130.7$, $S^\circ(H_2O) = 69.91$ (all in JK^{-1} mol^{-1})]

(*c*) $Na_2CO_3(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$

[$S^\circ Na_2CO_3 = 136.0$. $S^\circ(HCl) = 56.5$, $S^\circ(NaCl) = 115.13$, $S^\circ(H_2O) = 69.9$, $S^\circ(CO_2) = 213.74$ (all in JK^{-1} mol^{-1})]

65. Using $\Delta_f H^\circ$ and S_m° calculate the standard molar Gibbs energy of formation, $\Delta_f G^\circ$ for each of the following :

(*a*) $CS_2(l)$ (*b*) $N_2H_4(l)$

$\Delta_f H^\circ(CS_2) = 89.70$ kJ mol^{-1}, $\Delta_r S^\circ(CS_2) = 151.34$ JK^{-1} mol^{-1}

$\Delta_f H^\circ(N_2H_4) = 50.63$ kJ mol^{-1}, $\Delta_r S^\circ N_2H_2 = 121.21$ JK^{-1} mol^{-1}

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Answers to Practice Problems

61. 2.641 kJ

62. $\Delta G^\circ = -257.023$ kJ mol^{-1}. Since ΔG° is negative, the reaction is spontaneous.

63. -354.4 JK^{-1} mol^{-1}

64. (*a*) -549.4 JK^{-1} mol^{-1}, (*b*) -125.04 JK^{-1} mol^{-1} (*c*) 264.9 JK^{-1} mol^{-1}

65. (*a*) 44.60 kJ mol^{-1} (*b*) 14.51 kJ mol^{-1}

Hints & Solutions on page 78

add on

Conceptual Questions 3

CONCEPTUAL QA

Q.1. How does entropy change with
(*i*) increase in temperature, (*ii*) decrease in pressure ?

Ans. Entropy
(*i*) increases with increase in temperature.
(*ii*) increases with decrease of pressure (for gases).

Q.2. Is the entropy of the universe constant ?

Ans. No, entropy of the universe increases everyday.

Q.3. What is the value of change in entropy at equilibrium ?

Ans. At equilibrium, the change in entropy is zero, i.e. $\Delta S = 0$ (at equilibrium).

Q.4. Arrange water vapour, liquid water and ice in the order of increasing entropy :

Ans. ice < liquid water < water vapour.

Q.5. Do you expect ΔS to be +ve, –ve or zero for the reaction : $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.

Ans. ΔS should be negative because two different molecules (H_2 and I_2) would have more randomness than two same molecules (HI). Therefore, ΔS decreases.

Q.6. Place the following systems in order of increasing randomness :

(*a*) 1 mol of a gas X (*b*) 1 mol of a solid X (*c*) 1 mol of a liquid X. ***N.C.E.R.T.***

Ans. Order of increasing randomness :
1 mol of solid X < 1 mol of liquid X < 1 mol of gas X.

Q.7. Which of the following processes are accompanied by increase of entropy :

(*a*) Dissolution of iodine in a solvent

(*b*) HCl is added to $AgNO_3$ and a precipitate of AgCl is obtained.

(*c*) A partition is removed to allow two gases to mix. ***N.C.E.R.T.***

Ans. Increase of entropy : (a) and (c).

Q.8. Predict the sign of entropy change for each of the following changes of state :

(*a*) Hg (*l*) $\longrightarrow$ Hg(*g*)

(*b*) $AgNO_3(s) \longrightarrow AgNO_3\ (aq)$

(*c*) $I_2\ (g) \longrightarrow I_2\ (s)$

(*d*) C (graphite) $\longrightarrow$ C (diamond). ***N.C.E.R.T.***

Ans. (*a*) ΔS = +ve because liquid changes to more disordered gaseous state.
(*b*) ΔS = +ve because aqueous solution has more disorder than solid.
(*c*) ΔS = –ve because gas is changing to less disordered solid.
(*d*) ΔS = –ve because graphite has more disorder than diamond.

Q.9. Predict the entropy change (positive/negative) in the following :

(*i*) A liquid substance crystallizes into a solid.

(*ii*) Temperature of a crystal is increased.

(*iii*) $CaCO_3\ (s) \longrightarrow CaO\ (s) + O_2\ (g)$.

(*iv*) $N_2\ (g)$ (1 atm) $\longrightarrow N_2\ (g)$ (0.5 atm).

Ans. (*i*) Entropy decreases ; ΔS = –ve (*ii*) Entropy increases ; ΔS = +ve
(*iii*) Entropy increases ; ΔS = +ve (*iv*) Entropy increases : ΔS = +ve

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Q.10. If standard free energy change for a reaction is found to be zero, what is its equilibrium constant?

Ans. $\Delta G^\circ = -2.303\ RT \log K = 0$

$\therefore \quad \log K = 0$ or $K = 1$

Q.11. What is the value of ΔG at melting point of ice ?

Ans. At the melting point of ice $\Delta G = 0$ because the system : ice $\rightleftharpoons$ liquid at melting point is at equilibrium state.

Q.12. For a reaction both ΔH and ΔS are positive. Under what conditions will the reaction occur spontaneously ?

Ans. The reaction will occur spontaneously only when $T\Delta S > \Delta H$

$$\Delta G = \Delta H - T\Delta S = (+) - T(+)$$

For ΔG to be negative, $T\Delta S$ must be $> \Delta H$.

Q.13. Comment on the following statements :

(a) An exothermic reaction is always thermodynamically spontaneous.

(b) Reaction with $\Delta G^\circ < 0$ always have an equilibrium constant greater than 1. ***N.C.E.R.T.***

Ans. (a) Exothermic reactions are generally spontaneous because

(i) these are accompained by decrease of energy

(ii) the heat released is absorbed by the surroundings so that entropy of the surroundings increases and, therefore, ΔS_{total} is positive.

However, if ΔS system is –ve and T is very high, ΔG ($\Delta G = \Delta H - T\Delta S$) may be positive and the reaction may be non-spontaneous.

(b) $\Delta G < 0$ shows that the process is spontaneous. Equilibrium constant may not have value > 1 ($\Delta G^\circ = -RT \ln K$).

Q. 14. The standard molar entropy of $H_2O(l)$ is 70 JK^{-1} mol^{-1}. Will the standard molar entropy of $H_2O(s)$ be more or less than 70 JK^{-1} mol^{-1} ? ***(NCERT Exemplar Problem)***

Ans. Less than 70 JK^{-1} mol^{-1}, because ice is more ordered than $H_2O(l)$.

Q. 15. Which quantity out of $\Delta_r G$ or $\Delta_r G^\circ$ will be zero at equilibrium ? ***(NCERT Exemplar Problem)***

Ans. $\Delta_r G$ will be zero.

$\Delta_r G^\circ$ will be zero for $K = 1$ because $\Delta G^\circ = -RT\ ln\ K$

$\Delta_r G^\circ$ will be non-zero for other values of K.

Q. 16. Why is entropy of substance taken as zero at absolute zero of temperature ?

Ans. At absolute zero of temperature, there is complete orderly molecular arrangement in the crystalline substance. Therefore, there is no randomness at 0 K and entropy is taken to be zero.

Advanced Level PROBLEMS *Accelerate Your Potential (for JEE Advance)*

Problem 11. Calculate ΔG and ΔG° for the reaction :

$$A + B \rightleftharpoons C + D$$

at 27°C for which $K = 10^2$.

Solution $\Delta G = 0$ because reaction is at equilibrium.

$\Delta G^\circ = -2.303\ RT \log K$

$K = 10^2$, $T = 273 + 27 = 300$ K,

$R = 8.314\ JK^{-1}\ mol^{-1}$

$\therefore \quad \Delta G^\circ = -2.303\ (8.314\ JK^{-1}\ mol^{-1}) \times (300\ K) \times \log 10^2 = \mathbf{-11.48\ kJ}$

Problem 12. Calculate the value of $\log K_p$ for the reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

at 25°C. The standard enthalpy of formation of NH_3 is –46 kJ and standard entropies of $N_2(g)$, $H_2(g)$ and NH_3 (g) are 191, 130 and 192 JK^{-1} mol^{-1} respectively.

Solution $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$\Delta H^\circ = 2\,\Delta_f H^\circ (NH_3) - [\Delta_f H^\circ (N_2) + 3\Delta_f H^\circ (H_2)]$$

$$= 2 \times -46 = -92\ kJ$$

Now, $\Delta S^\circ = 2\,S^\circ (NH_3) - [S^\circ (N_2) + 3\,S^\circ (H_2)]$

$$= 2 \times 192 - [191 + 3 \times 130]$$

$$= -197\ JK^{-1} \text{ or } = -0.197\ kJ\ K^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -92 - 298 \times (-0.197)$$

$$= -33.294\ kJ = -33.294 \times 10^3\ J$$

Now, $\Delta G^\circ = -2.303\ RT \log K_p$

or $\log K_p = -\dfrac{\Delta G}{2.303\ RT}$

$$= -\frac{-33.294 \times 10^3}{2.303 \times 8.314 \times 298} = \mathbf{5.835.}$$

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Problem 13. **Sodium carbonate, Na_2CO_3 can be obtained by heating sodium hydrogen carbonate, $NaHCO_3$ as**

$2\,NaHCO_3\,(s) \rightarrow Na_2CO_3\,(s) + H_2O\,(g) + CO_2\,(g)$

The essential data are :

	$NaHCO_3$ (s)	Na_2CO_3 (s)	CO_2 (g)	H_2O(g)
$\Delta_f H°$ (kJ mol^{-1})	–947.7	–1130.9	–393.51	–241.82
$S_m°$ (J mol^{-1})	102.1	136	188.83	213.74

Calculate the temperature above which $NaHCO_3$ decomposes to give products at 1 bar.

Solution $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

$$\Delta_r H° = \Delta_f H°\,(Na_2CO_3) + \Delta_f H°\,(CO_2) + \Delta_f H°\,(H_2O) - 2\,\Delta_f H°\,(NaHCO_3)$$

$$= -1130.9 + (-393.51) + (-241.82) - 2 \times (-947.7)$$

$$= -1766.23 + 1895.4 = 129.17 \text{ kJ mol}^{-1}$$

$$\Delta_r S° = S_m°\,(Na_2CO_3) + S_m°\,(CO_2) + S_m°\,(H_2O) - 2\,S_m°\,(NaHCO_3)$$

$$= 136.0 + 188.83 + 213.74 - 2 \times 102.1$$

$$= 538.57 - 204.2 = 334.37 \text{ J K}^{-1} \text{ mol}^{-1}$$

Now at equilibrium, $\Delta_r G° = 0$ so that

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° = 0$$

$$\therefore T = \frac{\Delta_r H°}{\Delta_r S°} = \frac{129.17}{334.37 \times 10^{-3}} = 386 \text{ K}$$

$\therefore$ Reaction will be spontaneous above 386 K

Problem 14. **Show that the reaction:**

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ at 300 K is spontaneous and exothermic, when standard entropy change is –0.094 kJ mol^{-1} K^{-1}. The standard Gibbs energies of formation of CO_2 and CO are –394.4 and –137.2 kJ mol^{-1} respectively.

Solution $\Delta_r G° = \Delta_f G°$ (products) – $\Delta_f G°$ (reactants)

$$= \left[\Delta_f G°(CO_2)\right] - \left[\Delta_f G°(CO) + \frac{1}{2}\Delta_f G°(O_2)\right]$$

$$= -394.4 - [-137.2 + 0]$$

$$= -257.2 \text{ kJ}$$

Since $\Delta_r G°$ is negative, the reaction is spontaneous.

Now $\Delta G° = \Delta H° - T\Delta S$

$$-257.2 = \Delta H° - [300 \times (-0.094)]$$

$\therefore$ $\Delta H° = -257.2 - 28.2 = -285.4$ kJ

Since $\Delta H°$ is negative, the reaction is exothermic.

Problem 15. **The standard Gibbs energy change for the reaction**

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

is – 33.2 kJ mol^{-1} at 298 K.

(*a*) Calculate the equilibrium constant for the above reaction.

(*b*) What would be the equilibrium constant if the reaction is written as

$$\frac{1}{2}\,N_2(g) + \frac{3}{2}\,H_2(g) \rightleftharpoons NH_3(g)$$

(*c*) What will be the equilibrium constant if the reaction is :

$$NH_3(g) \rightleftharpoons \frac{1}{2}\,N_2(g) + \frac{3}{2}\,H_2(g)$$

Solution (*a*) For the reaction :

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

$\Delta G° = -33.2$ *k*J mol^{-1}

$$\log K = -\frac{\Delta G°}{2.303\,RT}$$

R = 8.314 JK^{-1} mol^{-1}, T = 298 K

$$\therefore \log K = -\frac{-33.2 \times 10^3 \text{ J mol}^{-1}}{2.303 \times (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}$$

$$= 5.82$$

or $K = \mathbf{6.6 \times 10^5}$.

(*b*) For the reaction :

$$\frac{1}{2}\,N_2(g) + \frac{3}{2}\,H_2(g) \longrightarrow NH_3(g)$$

$$\Delta G° = \frac{1}{2} \times -33.2 = -16.6 \text{ kJ mol}^{-1}$$

or $$\log K = \frac{-16.6 \times 10^3 \text{ J mol}^{-1}}{2.303 \times (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = 2.91$$

or $K = \mathbf{8.1 \times 10^2}$.

(*c*) For the reaction :

$$NH_3(g) \longrightarrow \frac{1}{2}\,N_2(g) + \frac{2}{3}\,H_2(g)$$

$$\Delta G° = -[-16.6 \text{ kJ mol}^{-1}] = 16.6 \text{ kJ mol}^{-1}$$

$$\log K = -\frac{16.6 \times 10^3 \text{ JK}^{-1} \text{ mol}^{-1}}{2.303 \times (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}$$

$$= -2.91$$

or $K = \mathbf{1.23 \times 10^{-3}}$.

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3. $\Delta U = q + w$

$\Delta U = -30 - 75 = \mathbf{-105\ J}$

4. $\Delta U = q + w$

$460 = 710 + w$

$w = 460 - 710 = \mathbf{-250\ J}$

5. $V_{initial} = \dfrac{nRT}{p}$

$= \dfrac{4 \times 0.082\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}{2.5\ \text{atm}}$

$= 39.36\ \text{L}$

$V_{final} = \dfrac{39.36}{2} = 19.68\ \text{L}$

$w = -p_{ext}\Delta V = -3 \times (19.68 - 39.36)$

$= 59.04\ \text{L atm}$

$= 59.04 \times 101.3\ \text{J} = \mathbf{5981\ J}$

For isothermal compression,

$\Delta U = 0$

$q = -w = \mathbf{-5981\ J}$

6. $w = -2.303\ n\ RT \log \dfrac{V_2}{V_1}$

Work done by system, $w = -4.620\ \text{kJ} = -4620\ \text{J}$

$\therefore \quad -4620 = -2.303 \times n \times 8.314 \times 300 \log \dfrac{20\ dm^3}{10\ dm^3}$

$4620 = 2.303 \times n \times 8.314 \times 300 \log 2$

$4620 = 1728.99\ n \quad \text{or} \quad n = \mathbf{2.67\ mol}.$

7. $\Delta H = \Delta U + \Delta n_g RT$

(*i*) $CH_3COOH(l) + 2O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$;

$\Delta H = -874\ \text{kJ}$

$\Delta n_g = 2 - 2 = 0$

$\therefore \quad -874\ \text{kJ} = \Delta U + 0 \times RT \text{ or } \Delta U = \mathbf{-874\ kJ}$

(*ii*) $CH_3CH_2OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$;

$\Delta H = -1363\ \text{kJ}$

$\Delta n_g = 2 - 3 = -1$

$-1363\ \text{kJ} = \Delta U - 1 \times 8.314 \times 10^{-3} \times 298$

$\Delta U = -1363 + 2.47 = \mathbf{-1360.53\ kJ.}$

8. $C_6H_5COOH(s) + \dfrac{15}{2} O_2(g) \longrightarrow 7CO_2(g) + 3H_2O(l)$

$\Delta n_g = 7 - \dfrac{15}{2} = -\dfrac{1}{2}$

$\Delta U = \Delta H - \Delta n_g RT$

$= -2546.0 - \left(-\dfrac{1}{2}\right) \times 8.314 \times 10^{-3} \times 298$

$\mathbf{-2544.8\ kJmol^{-1}.}$

9. $2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$

$\Delta n_g = 2 + 1 - 2 = 1$

$\Delta H = -163.15\ \text{kJ}$

$\Delta H = \Delta U + \Delta n_g RT$

or $\Delta U = \Delta H - \Delta n_g RT$

$= -163.15 - (1) \times 8.314 \times 10^{-3} \times 298$

$= -165.63\ \text{kJ}$

Moles of N_2O in 200 g $= \dfrac{200}{44} = 4.545$

ΔU for 2 mol of decomposition of $N_2O = -165.63\ \text{kJ}$

ΔU for 4.545 mol of decomposition of

$N_2O = \dfrac{-165.63 \times 4.545}{2}$

$= \mathbf{-376.39\ kJ}$

10. $\Delta T = 300.78 - 294.05 = 6.73°$

$q = C_v \times \Delta T$

$= 8.93 \times 6.73\ \text{kJ} = 60.1\ \text{kJ}$

Heat transferred to calorimeter = **60.1 kJ**

11. Heat capacity of water = Heat capacity of calorimeter

Heat gained by water = Heat lost by calorimeter

Heat lost by calorimeter $= C_v \times \Delta T$

$= m \times s \times \Delta T$

$= 125 \times 4.184 \times (296.5 - 286.4)$

$= 5282.3\ \text{J}$

$\therefore \quad q = \mathbf{5.28\ kJ}$

12. $q = C_v \times \Delta T$

$= -20.7 \times (299 - 298) = -20.7\ \text{kJ}$

$\therefore \quad \Delta U = -20.7\ \text{kJ mol}^{-1}$

Heat of combustion for 1 mol $= \dfrac{-20.7 \times 12.0}{1}$

$= \mathbf{-2.48 \times 10^2\ kJ\ mol^{-1}.}$

13. The enthalpy of formation of Fe_2O_3 corresponds to the reaction,

$2Fe(s) + \dfrac{3}{2} O_2(g) \longrightarrow Fe_2O_3(s) \qquad \Delta H = -824.2\ \text{kJ}$

$\therefore$ For the reaction,

$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s) \qquad \Delta H = 2 \times (-824.2)$

$= \mathbf{-1648.4\ kJ}$

14. For the reaction :

$4S(s) + 6O_2(g) \longrightarrow 4SO_3(g) \qquad \Delta H° = -1583.2\ \text{kJ}$

For the formation of SO_3, the equation is

$S(s) + \dfrac{3}{2} O_2(g) \longrightarrow SO_3(g) \quad \Delta_f H° = -\dfrac{1583.2}{4}$

$= \mathbf{-395.8\ kJ}$

15. For the reaction,

$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$

$\Delta H° = [\Delta_f H°(CO) + \Delta_f H°(H_2O)] - [\Delta_f H°(CO_2) + \Delta_f H°(H_2)]$

$= [-111.3 + (-241.8)] - [-393.5 + 0] = \mathbf{40.4\ kJ.}$

16. $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

$\Delta H° = [2\Delta_f H°(CO_2) + 3\ \Delta_f H°(H_2O)] - [\Delta_f H°(C_2H_5OH) + 3\ \Delta_f H°(O_2)]$

$= [2(-393.5) + 3(-285.8)] - [-277.0 + 3(0)]$

$= [-787 - 857.4] + 277 = \mathbf{-1367.4\ kJ.}$

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17. For the reaction,

$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$ $\Delta H^\circ = -1323$ kJ

$\Delta H^\circ = [2\,\Delta_f H^\circ(CO_2) + 2\Delta_f H^\circ(H_2O)] - [\Delta_f H^\circ(C_2H_4) + 3\Delta_f H^\circ(O_2)]$

$-1323 = [2 \times (-393.5) + 2 \times (-249.0)] - [\Delta_f H^\circ(C_2H_4) + 3(0)]$

$-1323 = [-787 - 498] - \Delta_f H^\circ(C_2H_4)$

$\Delta_f H^\circ(C_2H_4) = 1323 - 1285 =$ **38 kJ mol^{-1}.**

18. $2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$

$\Delta H^\circ = [4\Delta_f H^\circ(CO_2) + 6\,\Delta_f H^\circ(H_2O)] - [2\,\Delta_f H^\circ(C_2H_6) + 7\,\Delta_f H^\circ(O_2)]$

$= [4 \times (-94.1) + 6 \times (-68.3)] - [2 \times (-21.1) + 7(0)]$

$= -786.2 + 42.2 =$ **– 744.0 kcal.**

19. $2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2$

$\Delta_r H^\circ = [2\,\Delta_f H^\circ(H_2O) + 2\,\Delta_f H^\circ(SO_2)] - [2\,\Delta_f H^\circ(H_2S) + 3\,\Delta_f H^\circ(O_2)]$

$= [2 \times (-285.83) + 2 \times (-296.83)] - [2 \times (-20.60) + 3 \times 0]$

$= -1165.32 + 41.20$

$=$ **– 1124.12 kJ**

20. The fuel efficiency can be calculated from the amount of heat evolved for every gram of fuel consumed. This can be done by first calculating the heat of combustion of these hydrocarbons.

(*i*) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$\Delta_c H^\circ = [\Delta_f H^\circ(CO_2) + 2\Delta_f H^\circ(H_2O)] - [\Delta_f H^\circ(CH_4) + 2\,\Delta_f H^\circ(O_2)]$

$= [-393.5 + 2(-285.8)] - [(-74.8) + 0]$

$= -890.3$ kJ mol^1

Heat evolved per gram $= \dfrac{890.3}{16} = 55.64$ kJ g^{-1}.

(*ii*) $C_2H_6(g) + \dfrac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

$\Delta_c H^\circ = [2\Delta_f H^\circ(CO_2) + 3\Delta_f H^\circ(H_2O)] - [\Delta H^\circ(C_2H_6) + \dfrac{7}{2}\Delta_f H^\circ(O_2)]$

$= [2 \times (-393.5) + 3(-285.8)] - [-84.7 + 0]$

$= -1559.7$ kJ mol^{-1}

Heat evolved per gram $= \dfrac{1569.7}{30} = 51.99$ kJ g^{-1}

(*iii*) $C_4H_{10}(g) + \dfrac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$

$\Delta_c H^\circ = [4\Delta_f H^\circ(CO_2) + 5\Delta_f H^\circ(H_2O)] - [\Delta_f H^\circ(C_4H_{10}) + \dfrac{13}{2}\Delta_f H^\circ(O_2)]$

$= [4(-393.5) + 5(-285.8)] - [(-126.1) + 0]$

$= -2876.9$ kJ mol^{-1}

Heat evolved per gram $= \dfrac{2876.9}{58} = 49.6$ kJ g^{-1}

The decreasing order of fuel efficiency :

$CH_4 > C_2H_6 > C_4H_{10}$.

21. $C_{12}H_{22}O_{11}(s) + 12\,O_2(g) \longrightarrow 12\,CO_2(g) + 11H_2O(l) + 5645$ kJ

1 mol of sucrose = 342 g

(*i*) 1 mol or 342 g of sucrose on combustion liberate heat = 5645 kJ

51.3 g of sucrose on combustion liberate heat

$= \dfrac{5645 \times 51.3}{342} =$ **846.75 kJ**

(*ii*) Energy is needed to produce sucrose

342 g of sucrose require energy = 5645 kJ

5.472 g of sucrose require energy $= \dfrac{5645}{342} \times 5.472$

$=$ **90.32 kJ.**

22. Molecular mass of butane (C_4H_{10}) = 58

58g of butane on complete combustion give heat = 2658 kJ

11200g of butane on complete combustion give heat

$= \dfrac{2658 \times 11200}{58}$

$= 513268.9$ kJ

Since efficiency of combustion is 80%,

$\therefore$ Heat produced by 80% combustion of butane

$= \dfrac{513268.9 \times 80}{100}$

$= 410615$ kJ

The family need is 25000 kJ per day

25000 kJ of heat is used by family in = 1 day

410615 kJ of heat is used by family in $= \dfrac{410615}{25000}$

$=$ **16.4 days.**

23. The reaction is

$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$

Fuel mixture

$\Delta_r H^\circ$ for the reaction is

$\Delta_r H^\circ = [\Delta_f H^\circ(Al_2O_3) + 2\,\Delta_f H^\circ(Fe)] - [2\Delta_f H^\circ(Al) + \Delta_f H^\circ(Fe_2O_3)]$

$= [-399.0 + 2(0)] - [2(0) + (-199.0)]$

$= -200$ kcal.

Mol. wt. of fuel mixture $= 2 \times 27 + (2 \times 57 + 48) = 214$ g

Fuel value $= \dfrac{200}{214} =$ **0.9346 kcal/g**

Calculation of fuel value per cc

Volume of Al $= \dfrac{54}{2.7} = 20$ cc

Volume of $Fe_2O_3 = \dfrac{160}{5.2} = 30.77$ cc

Total volume $= 20 + 30.77 = 50.77$ cc

Fuel value per cc $= \dfrac{200}{55.77} =$ **3.94 kcal/cc.**

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24. The equations are :

(*i*) $CH_3COOH(l) + 2O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$
$\Delta H = -867$ kJ

(*ii*) $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

(*iii*) $H_2(g) + 1/2\ O_2(g) \longrightarrow H_2O(l)$ $\Delta H = -285.9$ kJ

The required equation is

$2C(s) + 2H_2(g) + O_2(g) \longrightarrow CH_3COOH(l)$
$\Delta H = ?$

Multiply eq. (*ii*) by 2 and (*iii*) by 2 and add

$2 \times (ii)$ $2C(s) + 2O_2(g) \longrightarrow 2CO_2(g)$
$\Delta H = -787.0$ kJ

$2 \times (iii)$ $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$
$\Delta H = -571.8$ kJ

Adding (*iv*) $2C(s) + 2H_2(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$
$\Delta H = -1358.8$ kJ

Subtract eq. (*i*) from eq. (*iv*)

(*i*) $CH_3COOH(l) + 2O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$
$\Delta H = -867.0$ kJ

Subtracting $2C(s) + 2H_2(g) + O_2(g) \longrightarrow CH_3COOH(l)$
$\Delta H = -$ **491.8 kJ.**

25. The equations are :

(*i*) $C_3H_8(g) + 5\ O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$
$\Delta H = -2220.2$ kJ

(*ii*) $C(s) + O_2(g) \longrightarrow CO_2(g)$
$\Delta H = -393.5$ kJ

(*iii*) $H_2(g) + 1/2\ O_2(g) \longrightarrow H_2O(l)$
$\Delta H = -285.8$ kJ

The required equation is

$3C(s) + 4H_2(g) \longrightarrow C_3H_8(g)$ $\Delta H = ?$

Multiply eq. (*ii*) by 3 and eq. (*iii*) by 4

(*ii*) $\times 3$ $3C(s) + 3O_2(g) \longrightarrow 3CO_2(g)$
$\Delta H = -1180.5$ kJ

(*iii*) $\times 4$ $4H_2(g) + 2O_2(g) \longrightarrow 4H_2O(l)$
$\Delta H = -1143.2$ kJ

Add (*iv*) $3C(s) + 4H_2(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$
$\Delta H = -2323.7$ kJ

Subtract eq. (*i*) from eq. (*iv*)

(*i*) $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$
$\Delta H = -2220.2$ kJ

Subtract $3C(s) + 4H_2(g) \longrightarrow C_3H_8(g)$
$\Delta H = -$ **103.5 kJ.**

26. The equations are :

(*i*) $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$
$\Delta H = -1368.0$ kJ

(*ii*) $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

(*iii*) $H_2(g) + 1/2\ O_2(g) \longrightarrow H_2O(l)$ $\Delta H = -286.0$ kJ

The required equation is

$2C(s) + 3H_2(g) + 1/2O_2(g) \longrightarrow C_2H_5OH(l)$
$\Delta H = ?$

Multiply eq. (*ii*) by 2 and (*iii*) by 3 and add

(*ii*) $\times 2$ $2C(s) + 2O_2(g) \longrightarrow 2CO_2(g)$
$\Delta H = -787.0$ kJ

(*iii*) $\times 3$ $3H_2(g) + 3/2O_2(g) \longrightarrow 3H_2O(l)$
$\Delta H = -858.0$ kJ

Adding (*iv*)

$2C(s) + 3H_2(g) + 7/2O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$
$\Delta H = -1645$ kJ

Subtract eq. (*i*) from eq. (*iv*)

$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$
$\Delta H = -1368.0$ kJ

Subtracting $2C(s) + 3H_2(g) + 1/2\ O_2(g) \longrightarrow C_2H_5OH(l)$
$\Delta H = -$ **277.0** kJ

27.

(*i*) $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ $\Delta H = -571.8$ kJ

$CH_4(g) + 2O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$
$\Delta H = -890.3$ kJ

The required equation is

$C(s) + 2H_2(g) \longrightarrow CH_4(g)$ $\Delta H = ?$

The required equation can be obtained as (*i*) + (*ii*) – (*iii*)
$\Delta H =$ **– 75.0 kJ**

28.

(*i*) $S(rhombic) + O_2(g) \longrightarrow SO_2(g)$
$\Delta H° = -294.1$ kJ

(*ii*) $S(monoclinic) + O_2(g) \longrightarrow SO_2(g)$
$\Delta H° = -295.4$ kJ

The required equation is

$S(monoclinic) \longrightarrow S(rhombic)$ $\Delta H = ?$

This can be obtained by subtracting eq. (*i*) from eq.(*ii*)

$\Delta H° = -295.4 - (-294.1) =$ **– 1.3 kJ.**

29. We are given

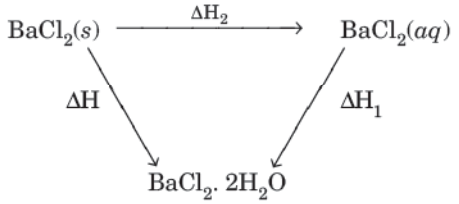
(*i*) $BaCl_2.\ 2H_2O + aq \longrightarrow BaCl_2(aq)$ $\Delta H_1 = 8.8$kJ

(*ii*) $BaCl_2 + aq \longrightarrow BaCl_2\ (aq)$ $\Delta H_2 = -20.6$kJ

The required equation is

$BaCl_2(s) + 2H_2O(l) \longrightarrow BaCl_2.\ 2H_2O(s)$ $\Delta H = ?$

The process of hydration may be expressed as :



According to Hess' law,

$\Delta H + \Delta H_1 = \Delta H_2$

$\Delta H + 8.8$ kJ $= -20.6$ kJ

or $\Delta H = -20.6 - 8.8 =$ **– 29.4 kJ.**

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Solution File

30.

(*i*) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$
$\Delta H = -1409.5$ kJ

(*ii*) $C_2H_6(g) + 7/2\ O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$
$\Delta H = -1558.3$ kJ

(*iii*) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$ $\Delta H = -285.6$ kJ

The required equation is
$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$ $\Delta H = ?$
Add eq. (*i*) and (*iii*)

(*iv*) $C_2H_4(g) + H_2(g) + \frac{7}{2} O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$
$\Delta H = -1695.1$ kJ

Subtract eq. (*ii*) from eq. (*iv*)

(*ii*) $C_2H_6(g) + 7/2\ O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$
$\Delta H = -1558.3$ kJ

Subtracting $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$
$\Delta H = -$ **136.8 kJ mol^{-1}**

31.

(*i*) $K(s) + H_2O(l) + (aq) \longrightarrow KOH(aq) + \frac{1}{2} H_2(g)$
$\Delta H^\circ = -200.8$ kJ

(*ii*) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$ $\Delta H^\circ = -286.3$ kJ

(*iii*) $KOH(s) + (aq) \longrightarrow KOH(aq)$ $\Delta H^\circ = -58.6$ kJ

The required equation is

$K(s) + \frac{1}{2} H_2(g) + \frac{1}{2} O_2(g) \longrightarrow KOH(s)$ $\Delta H^\circ = ?$

Add eq. (*i*) and eq. (*ii*) and subtract eq. (*iii*)

$\Delta H^\circ = -200.8 + (-286.3) - (-58.6) =$ **-428.5 kJ mol^{-1}**

32. The required equation is

$4C(s) + 5H_2(g) \longrightarrow C_4H_{10}(g)$

The given equations are :

(*i*) $C_4H_{10}(g) + 13/2\ O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$
$\Delta H = -2878.7$ kJ

(*ii*) $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

(*iii*) $H_2(g) + ½\ O_2(g) \longrightarrow H_2O(l)$ $\Delta H = -285.8$ kJ

For calculating the required equation
Eq. (*ii*) × 4 + eq. (*iii*) × 5 – eq. (*i*)

$\therefore \Delta H = 4(-393.5) + 5(-285.5) - (-2878.7)$
$= -1574.0 - 1427.5 + 2878.7 =$ **-122.8 kJ mol^{-1}**

33. The required equation is

$NO(g) + \frac{1}{2} O_2(g) \longrightarrow NO_2(g)$ $\Delta H^\circ = ?$

The given equations are :

(*i*) $\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \longrightarrow NO(g)$; $\Delta H^\circ = 90.7$ kJ

(*ii*) $\frac{1}{2} N_2(g) + O_2(g) \longrightarrow NO_2(g)$; $\Delta H^\circ = 34.0$ kJ

For calculating the required equation subtract eq. (*i*) from eq. (*ii*)

$\Delta H^\circ = 34 - 90.7 =$ **-56.7 kJ mol^{-1}**

34. The given equations are :

(*i*) $C_2H_2(g) + \frac{5}{2} O_2(g) \longrightarrow 2CO_2(g) + H_2O(g)$
$\Delta H = -310.62$ kcal

(*ii*) $C(\text{graphite}) + O_2 \longrightarrow CO_2(g)$ $\Delta H = -94.05$ kcal

(*iii*) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$ $\Delta H = -68.32$ kcal

The required equation is
$2C(\text{graphite}) + H_2(g) \longrightarrow C_2H_2(g)$ $\Delta H = ?$
Multiply eq. (*ii*) by 2 and add eqn (*iii*) and (*ii*)

$2C(\text{graphite}) + 2O_2(g) \longrightarrow 2CO_2(g)$ $\Delta H = -188.10$ kcal

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$ $\Delta H = -68.32$ kcal

(*iv*) $2C(\text{graphite}) + H_2(g) + \frac{5}{2} O_2(g) \longrightarrow 2CO_2(g) + H_2O(g)$
$\Delta H = -256.42$ kcal

Subtract eqn (*i*)

(*i*) $C_2H_2(g) + \frac{5}{2} O_2(g) \longrightarrow 2CO_2(g) + H_2O(g)$
$\Delta H - 310.62$ kcal

Subtracting $2C(\text{graphite}) + H_2(g) \longrightarrow C_2H_2(g)$

$\Delta H = 54.20$ kcal.

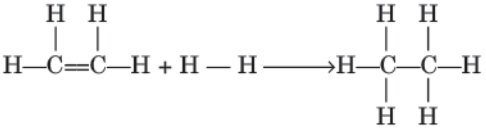
35. For the reaction

$H—H(g) + \frac{1}{2}(O = O)(g) \longrightarrow 2O—H(g)$

ΔH = (Bond enthalpy of H—H) + ½(Bond enthalpy of O = O) – 2 (Bond enthalpy of O —H)
$= 433 + ½(492) - 2(464) = 433 + 246 - 928$
$=$ **-249 kJ.**

36. For the reaction,

$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6$



$\Delta H = 4$ (B.E. of C—H) + (B.E. of C=C) + (B.E. of H—H) – 6 (B.E. of C—H) – (B.E. of C—C)
$= 4(413) + 615 + 433 - 6(413) - 347 =$ **-125 kJ.**

37. $HCl(g) \longrightarrow H(g) + Cl(g)$ $\Delta H^\circ = ?$

$\Delta H^\circ = \Sigma\Delta_f H^\circ$ (products) $- \Sigma\Delta_f H^\circ$ (reactants)
$= \Delta_f H^\circ(H) + \Delta_f H^\circ(Cl) - \Delta_f H^\circ(HCl)$

$\Delta_f H^\circ(H) = \frac{1}{2}(435.4) = 217.7$ kJ mol^{-1}

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$$\Delta_f H°(Cl) = \frac{1}{2}(242.8) = 121.4 \text{ kJ mol}^{-1}$$

$$\therefore \quad \Delta_f H°(HCl) = 217.7 + 121.4 - (-92.2) = \mathbf{431.3\ kJ}$$

38.

$$\Delta_r H° = \text{B.E.}\ (\text{H—C(H)(H)—C(H)(H)—C(H)(H)—H}) + 5\ \text{B.E.}\ (O = O)$$
$$- 3\ [\text{B.E.}\ (O = C = O) - 4\ \{\text{B.E.}\ (H—O—H)\}]$$
$$= 2\ [\text{B.E.}\ (C—C)] + 8\ [\text{B.E.}\ (C—H)] + 5\ \text{B.E.}\ (O = O)$$
$$- 6\ [\text{B.E.}\ (C = O) - 8\ \text{B.E.}\ (O - H)]$$
$$- 1662 = 2 \times 347 + 8 \times 414 + 5\ \text{B.E.}\ (O = O) - 6 \times 741 - 8 \times 464$$
$$- 1662 = 694 + 3312 + 5\ \text{B.E.}\ (O = O) - 4446 - 3712$$
$$5\ \text{B.E.}\ (O = O) = 2490 \text{ kJ mol}^{-1}$$
$$\text{B.E.}\ (O = O) = \mathbf{498\ kJ\ mol^{-1}}.$$

39. Molar enthalpy of vaporisation
$$= 2.275 \times 18 = 40.95 \text{ kJ mol}^{-1}$$
$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T} = \frac{40.95 \times 10^3}{373} = \mathbf{109.78\ J\ K^{-1} mol^{-1}}$$

40. $\Delta_{melting} S = \dfrac{\Delta_{melting}H}{T}$

or $T = \dfrac{\Delta_{melting}H}{\Delta_{melting}S} = \dfrac{30.4 \times 10^3}{28.4} = \mathbf{1070.4\ K}$

41. $\Delta_{fus}S = \dfrac{\Delta_{fus}H}{T_{(m.pt)}}$ $(T_{mpt} = 273 - 102 = 171\ K)$

or $= \dfrac{6400}{171} = \mathbf{37.4\ J\ K^{-1}\ mol^{-1}}$

$\Delta_{vap}S = \dfrac{\Delta_{vap}H}{T_{(b.pt)}}$ $(T_{b.pt} = 273 - 34 = 239\ K)$

$= \dfrac{20400}{239} = \mathbf{85.3\ JK^{-1}\ mol^{-1}}$

42. $\Delta_{vap}S = \dfrac{\Delta_{vap}H}{T}$

or $\Delta_{vap}H = \Delta_{vap}S \times T$ $(T = 273 + 56 = 329\ K)$
$= 93.0 \times 329\ K = 30597 \text{ J mol}^{-1}$

Heat required to vaporise 1 mole (58 g) of acetone
$= 30597$ J

Heat required to vaporise 1 g of acetone

$= \dfrac{30597}{58} = \mathbf{527.5\ J}$

43. (*i*) $\Delta_{vap}S = \dfrac{\Delta_{vap}H}{T}$ $(T = 273 + 80.1 = 353.1\ K)$

or $= \dfrac{30.8 \times 10^3}{353.1} = \mathbf{87.2\ JK^{-1}\ mol^{-1}}$

(*ii*) Since $\Delta_{cond}H = -\Delta_{vap}H$
$\Delta_{cond}S = \mathbf{-87.2\ J\ K^{-1}\ mol^{-1}}.$

44. $T = \dfrac{\Delta_{vap}H}{\Delta_{vap}S}$

$= \dfrac{40.73 \times 10^3 \text{ J mol}^{-1}}{109 \text{ J K}^{-1} \text{ mol}^{-1}} = \mathbf{373.67\ K}$

45. $\Delta_{vap}S = \dfrac{\Delta_{vap}H}{T}$

$= \dfrac{29.0 \times 10^3 \text{ J mol}^{-1}}{341.7\ K}$

$= \mathbf{84.87\ JK^{-1}mol^{-1}}$

46. ΔH = Lattice energy – Hydration energy
$= 777.8 - 774.1 = 3.7 \text{ kJ mol}^{-1}$
$\Delta S = 43 \times 10^{-3} \text{ kJ mol}^{-1}$, $T = 298\ K$
$\Delta G = \Delta H - T\Delta S$
$\Delta G = 3.7 - 298\ (43 \times 10^{-3})$
$= 3.7 - 12.81 = \mathbf{-9.11\ kJ\ mol^{-1}}$

47. The spontaneity of a reaction can be decided by calculating ΔG.
For reaction A :
$\Delta G = \Delta H - T\Delta S$
$\Delta H = -10.5 \times 10^3 \text{ J mol}^{-1}$, $\Delta S = 31 \text{ JK}^{-1} \text{ mol}^{-1}$
$\Delta G = -10.5 \times 10^3 - 298 \times 31$
$= -10500 - 9238 = -19738 \text{ J mol}^{-1}$
Since ΔG is negative, reaction will be spontaneous at 298 K.
For reaction B :
$\Delta H = -11.7 \times 10^3 \text{ J mol}^{-1}$, $\Delta S = -105 \text{ JK}^{-1} \text{ mol}^{-1}$
$\Delta G = -11.7 \times 10^3 - 298\ (-105)$
$= -11700 + 31290 = \mathbf{19520\ J\ mol^{-1}}$
Since ΔG is positive, reaction will be non-spontaneous at this temperature.

48. At equilibrium,
$\Delta G = \Delta H - T\Delta S = 0$
or $\Delta H = T\Delta S$
$108.4 \text{ kJ} = T\ (190 \times 10^{-3} \text{ kJ K}^{-1})$
or $T = \dfrac{108.4}{190 \times 10^{-3}} = \mathbf{570.5\ K}$

Reaction will become spontaneous at temperature higher than 570.5 K.

49. $\Delta H = T\Delta S$
$40 \text{ kJ} = T\ (0.02 \text{ kJ K}^{-1})$
$T = \dfrac{40}{0.02} = \mathbf{2000\ K}$

50. For the reaction :
$$2NO\ (g) + O_2\ (g) \longrightarrow 2NO_2(g)$$
$$\Delta G° = 2\Delta_f G°\ (NO_2) - [2\Delta_f G°(NO) + \Delta_f G°(O_2)]$$

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$= 2 \times 51.84 - 2 \times 86.69 - 0$
$= 103.68 - 173.38$
$= \mathbf{-69.7\ kJ\ mol^{-1}}$

51. $\Delta_r G^\circ = 6\Delta_f G^\circ (CO_2) + 6\Delta_f G^\circ (H_2O) - [\Delta_f G^\circ (C_6H_{12}O_6) + 6\ \Delta_f G^\circ (O_2)]$
$= 6 \times -394.4 + 6 \times -237.2 - (-910.2)$
$= -2366.4 - 1423.2 + 910.2$
$= \mathbf{-2879.4\ kJ\ mol^{-1}}$

52. $\Delta G^\circ = -2.303\ RT \log K$
$K = 1.55 \times 10^{15}$
$\Delta G^\circ = -2.303 \times (8.314\ JK^{-1}) \times (298\ K) \log 1.55 \times 10^{15}$
$= -5705.8 \times (15.1903) = \mathbf{-86.7\ kJ\ mol^{-1}}$

53. $\Delta G^\circ = -2.303\ RT \log K$
$K = 73,\ T = 273 + 25 = 298\ K$
$\Delta G^\circ = -2.303 \times (8.314\ JK^{-1}\ mol^{-1}) \times (298\ K) \log 73$
$= -5705.8 \times 1.863 = \mathbf{-10.63\ kJ\ mol^{-1}}$

54. $\Delta G^\circ = [2\Delta G^\circ_f (H_2) + \Delta G^\circ_f (O_2)] - [2\Delta G^\circ_f (H_2O)]$
$= [2 \times (0) + (0)] - 2 \times (-237.2)$
$= 474.4\ kJ$
$\Delta G^\circ = -2.303\ RT \log K$
$\Delta G^\circ = 474.4\ kJ = 474400\ J,\ R = 8.314\ JK^{-1}\ mol^{-1},\ T = 298\ K$

$$\log K = -\frac{\Delta G^\circ}{2.303\ RT} = \frac{474400}{2.303 \times 8.314 \times 298}$$

$\log K = -83.143$
$K = \mathbf{7.19 \times 10^{-84}}$

55. $\Delta G^\circ = -2.303\ RT \log K$
$= -2.303 \times (8.314\ JK^{-1}\ mol^{-1}) \times (298\ K) \log 4$
$= -570.8 \times 0.6020$
$= \mathbf{-3.434\ kJ\ mol^{-1}}$

56. We know
$\Delta G^\circ = -2.303\ RT \log K$
$K = 1.8 \times 10^{-7},\ R = 8.314\ JK^{-1}\ mol^{-1},\ T = 298\ K$
$\Delta G^\circ = -2.303 \times 8.314 \times 298 \times \log 1.8 \times 10^{-7}$
$= 38.484\ kJ\ mol^{-1}$
Now, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\text{or}\quad \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$= \frac{28.40 - 38.484}{298}$$

$= -0.0338\ kJ\ mol^{-1}\ K^{-1}$
$= \mathbf{-33.8\ J\ mol^{-1}\ K^{-1}}$

57. ΔH° for the reaction
$= [\Delta H^\circ_f (CO) + \Delta H^\circ_f (H_2)] - [\Delta H^\circ_f (C) + \Delta H^\circ_f (H_2O)]$
$= [-110.5 + 0] - [0 + (-286.0)]$
$= 175.5\ kJ\ mol^{-1}$
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
$= 175.5 - 298 \times 252.6 \times 10^{-3}$
$= 100.225\ kJ\ mol^{-1}$
Now, $\Delta G^\circ = -2.303\ RT \log K$

$$\text{or}\quad \log K = -\frac{\Delta G^\circ}{2.303\ RT}$$

$$= -\frac{100225}{2.303 \times 8.31 \times 298} = -17.565$$

or $K = \mathbf{2.72 \times 10^{-18}}$

58. $\Delta G^\circ = -2.303\ RT \log K$

$$\text{or}\quad \log K = -\frac{\Delta G^\circ}{2.303\ RT}$$

$\Delta G^\circ = -474.78\ kJ\ mol^{-1},\ R = 8.314\ JK^{-1}\ mol^{-1}$
$T = 298\ K$

$$\therefore\quad \log K = -\frac{-474.78 \times 10^3\ J\ mol^{-1}}{2.303 \times 8.314 \times 298}$$

$= \mathbf{83.21}$

59. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
$\Delta S^\circ = -70.8\ JK^{-1}\ mol^{-1},\ T = 298\ K$

$$\Delta H^\circ = \Delta_f H^\circ (NO_2) - \{\Delta_f H^\circ (NO) + \frac{1}{2}\ \Delta_f H^\circ (O_2)\}$$

$$= 33.8 - 90.4 - \frac{1}{2}\ (0)$$

$= -56.6\ kJ\ mol^{-1}$
$\therefore\quad \Delta G^\circ = -56.6 \times 10^3 - 298 \times (-70.8)$
$= -56600 + 21098.4$
$= -35501.6\ J\ mol^{-1}$

Now $\log K = -\dfrac{\Delta G^\circ}{2.303RT}$

$$= -\frac{-35501.6}{2.303 \times 8.314 \times 298} = 6.222$$

or $K = \mathbf{1.67 \times 10^6}$

60. For the reaction :
$Br_2 (l) + Cl_2 (g) \longrightarrow 2BrCl (g)$
$\Delta H^\circ = 29.3\ kJ\ mol^{-1},\ \Delta S^\circ = 104.1\ JK^{-1}\ mol^{-1}$
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
$= 29.3 \times 10^3 - 298 \times 104.1$
$= 29300 - 31021.8$
$= -1721.8\ J\ mol^{-1}$

Now $\log K = -\dfrac{\Delta G^\circ}{2.303\ RT}$

$$= -\frac{-1721.8}{2.303 \times 8.314 \times 298}$$

$= 0.3018$
or $\mathbf{K = 2.003}$

61. $\Delta S^\circ = 2S^\circ (HI) - [S^\circ (H_2) + S^\circ (I_2)]$
$= 165.3\ JK^{-1}\ mol^{-1}$
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
$= 51.9 \times 10^3 - 298\ (165.3)$
$= \mathbf{2.641\ kJ\ mol^{-1}}$

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62. $\Delta S^\circ = S^\circ (CO_2) - [S^\circ (CO) + \frac{1}{2} S^\circ (O_2)]$

$= -86.5\ JK^{-1}\ mol^{-1}$

$\Delta G^\circ = -282.8 \times 10^3 - 298\ (-86.5)$

$= \mathbf{-257.023\ kJ\ mol^{-1}}$

63. $\Delta_r S^\circ = S^\circ (NH_2CONH_2) + S^\circ (H_2O) - [2S^\circ (NH_3) + S^\circ (CO_2)]$

$= 174.0 + 69.8 - [2 \times 192.3 + 213]$

$= \mathbf{-354.4\ JK^{-1}\ mol^{-1}}$

65. (*a*) $\Delta_f G^\circ = \Delta_f H^\circ - T\Delta_r S^\circ$

$= 89.70 \times 10^3 - 298\ (151.34)$

$= \mathbf{44.6\ kJ\ mol^{-1}}$

(*b*) $\Delta_f G^\circ = \Delta_f H^\circ - T\Delta_r S^\circ$

$= 50.63 \times 10^3 - 298\ (121.21)$

$= \mathbf{14.51\ kJ\ mol^{-1}}$.

Chapter Summary

Key Terms

- **System.** A part of universe which is under investigation.
- **Surroundings.** The rest of the universe which is not a part of the system.
- **State of the system.** The conditions of existence of a system when its macroscopic properties have definite values.
- **State functions.** The thermodynamic quantities which depend only on the initial and final state of the system.
- **Internal energy (U).** The energy associated with the system at a particular conditions of temperature and pressure.
- **Internal energy change (ΔU).** It is a measure of heat change occurring during the process at constant temperature and constant volume. $q_v = \Delta U$
- **Enthalpy (ΔH).** It is sum of internal energy and pressure-volume energy of the system at a particular temperature and pressure. It is also called heat content ($H = E + pV$)

QUICK CHAPTER ROUND UP

System

Open system
- can exchange matter and energy with surroundings

Closed system
- can exchange energy and not matter with surroundings

Isolated system
- can neither exchange energy nor matter with surroundings

Properties of system

Intensive
- independent of amount of substance
- ▸ T, P, viscosity, specific heat capacity

Extensive
- depends upon amount of substance
- ▸ mass, volume, energy, enthalpy, entropy

Processes

named according to constant conditions

Constant temperature	⇒	Isothermal
Constant pressure	⇒	Isobaric
Constant volume	⇒	Isochoric
Constant heat	⇒	Adiabatic.

Sign Conventions for Heat (*q*) and Work (*w*)
Heat absorbed by the system = *q* positive.
Heat evolved by the system = *q* negative.
Work done on the system = *w* positive.
Work done by the system = *w* negative.

- **State-function**
  - Thermodynamic quantity which depends only on the initial and final state of the system.

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q_V (Heat absorbed or evolved at constant V) = U
q_P (Heat absorbed or evolved at constant p) = H

$H = U + pV$

$\Delta H = \Delta U + p\Delta V$ (at constant p)

or $\Delta H = \Delta U + \Delta n_g RT$

(Δn_g = Change in gaseous moles)

- **Law of conservation of energy.** It states that the energy of the universe always remains constant during chemical and physical changes.

  $\Delta U = q + w$
- Internal energy of an ideal gas depends only on temperature. Therefore, in an isothermal process involving ideal gas,

  $\Delta U = 0$.
- Work of expansion, $w = -p\Delta V$.

  Work of expansion in vacuum, $p_{ext} = 0$, $w = 0$
- First law of thermodynamics

  $\Delta U = q + w$ or $\Delta U = q - p\Delta V$

Enthalpy change

$\Delta H^\theta = \Sigma H^\theta$ (products) - ΣH^θ (reactants)

- **Enthalpy of reaction.** The enthalpy change accompanying a chemical reaction when the number of moles of reactants react to give the products as given by the balanced chemical equation.
- **Standard enthalpy of formation ($\Delta_f H°$).** The enthalpy change accompanying the formation of one mole of the compound from its elements, all the substances being in their standard states (1 atm pressure and 25°C temperature).

As a convention, the $\Delta_f H°$ of every element is assumed to be zero.

- **Enthalpy of combustion ($\Delta_c H°$).** The amount of heat change when 1 mole of the substance is completely burnt in excess of oxygen or air. **$\Delta_c H°$ is always negative.**
- **Enthalpy of solution.** The enthalpy change when one mole of a substance is dissolved in large excess of solvent so that further dilution does not give any further enthalpy change.
- **Enthalpy of neutralisation.** The enthalpy change when 1 mole of H^+ of an acid is completely neutralised by a base or vice versa in dilute solution. The enthalpy of neutralisation of all strong acids by strong bases is always equal to **57.1 kJ** irrespective of the nature of the acid or the base.
- **Enthalpy of hydration.** The enthalpy change during the hydration of 1 mole of anhydrous salt to a specific hydrate.

- **Hess's law.** The enthalpy change in a particular reaction is the same whether the reaction takes place in one step or in a number of steps.

$$\Delta S^\ominus = \frac{q_{rev}}{T}$$

$$\Delta S^\ominus_{vap} = \frac{\Delta_{vap} H}{T_b} \quad (T_b = \text{Boiling point})$$

$$\Delta S^\ominus_{fusion} = \frac{\Delta_{fus} H}{T_m} \quad (T_m = \text{Melting point})$$

$$\Delta S^\ominus = \Sigma S^\theta_{(products)} - \Sigma S^\theta_{(reactants)}$$

$$S_{Universe} = \Delta S_{Sys} + \Delta S_{Surr}$$

In a reversible process, $\Delta S_{Universe} = 0$

$\therefore \quad \Delta S_{Sys} = -\Delta S_{Surr}$

In a irreversible process,

$\Delta S_{Universe} > 0$

$$\Delta G^\ominus = \Delta H - T\Delta S^\ominus$$

$$\Delta G^\ominus = -2.303\ RT \log K$$

(K is equilibrium constant)

$$\Delta G^\ominus = -nFE^\ominus_{cell}$$

Conditions of ΔG

$\Delta G^\ominus$ = –ve	Spontaneous process
$\Delta G^\ominus = 0$	Equilibrium state
$\Delta G^\ominus$ = +ve	Non-spontaneous process

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NCERT FILE Solved

NCERT Textbook Exercises

Q. 1. Choose the crrect answer. A thermodynamic state function is a quantity

(*i*) used to determine heat changes

(*ii*) whose value is independent of path

(*iii*) used to determine pressure volume work

(*iv*) whose value depends on temperature only.

Ans. (*ii*)

Q. 2. For the process to occur under adiabatic conditions, the correct condition is :

(*i*) $\Delta T = 0$ (*ii*) $\Delta p = 0$

(*iii*) $q = 0$ (*iv*) $w = 0$

Ans. (*iii*)

Q. 3. The enthalpies of all elements in their standard states are :

(*i*) unity

(*ii*) zero

(*iii*) $q = 0$

(*iv*) different for each element

Ans. (*ii*)

Q. 4. ΔU° of combustion of methane is – X kJ mol^{-1}. The value of ΔH is

(*i*) $= \Delta U^\circ$ (*ii*) $> \Delta U^\circ$

(*iii*) $< \Delta U^\circ$ (*iv*) $= 0$

Ans. (*iii*)

Q. 5. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are – 890.3 kJ mol^{-1}, –393.5 kJ mol^{-1} and – 285.8 kJ mol^{-1} respectively. Enthalpy of formation of CH_4 (g) will be

(*a*) – 74.8 kJ mol^{-1} (*b*) – 52.27 kJ mol^{-1}

(*c*) + 74.8 kJ mol^{-1} (*d*) + 52.26 kJ mol^{-1}

Ans. (*a*) : Given equation are :

(*i*) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$\Delta H = -890.3$ kJ mol^{-1}

(*ii*) $C(s) + O_2(g) \longrightarrow CO_2(g)$

$\Delta H = -393.5$ kJ mol^{-1}

(*iii*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$

$\Delta H = -285.8$ kJ mol^{-1}

Required equation is :

$C(s) + 2H_2(g) \longrightarrow CH_4(g)$ $\Delta H = ?$

Eq. (*ii*) + 2 × Eq. (*iii*) – Eq (*i*) gives the required equation :

$\Delta H = -393.5 + 2(-285.8) - (-890.3)$

$= -74.8$ kJ mol^{-1}

Q. 6. A reaction, $A + B \longrightarrow C + D + q$ is found to have a positive entropy change. The reaction will be

(*a*) possible at high temperature

(*b*) possible only at low temperature

(*c*) not possible at any temperature

(*d*) possible at any temperature

Ans. (*d*)

Q. 7. In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process ?

Ans. Heat absorbed by the system = 701 J

or q = 701 J

Work done by the system = 394 J

or w = – 394 J

According to first law of thermodynamics

$\Delta U = q + w$

$\Delta U = 701 - 394 =$ **307 J**

Q. 8. The reaction of cyanamide, NH_2CN (*s*), with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be –742.7 kJ mol^{-1} at 298 K. Calculate enthalpy change for the reaction at 298 K.

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l)$$

Ans. *Refer Solved Example 21. (Page 22).*

Q. 9. Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.

Ans. *Refer Solved Example 19. (Page 20).*

Q. 10. Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at –10.0°C. $\Delta_{fus}H = 6.03$ kJ mol^{-1} at 0°C.

C_p [$H_2O(l)$] = 75.3 J mol^{-1}K^{-1}

C_p [$H_2O(s)$] = 36.8 J mol^{-1}K^{-1}

Ans. *Refer Advanced Level Problems 1. (Page 50).*

Q. 11. Enthalpy of combustion of carbon to CO_2 is –393.5 kJ mol^{-1}. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

Ans. *Refer Solved Example 12. (Page15).*

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Q. 12. Enthalpies of formation of $CO(g)$, $CO_2(g)$, $N_2O(g)$ and $N_2O_4(g)$ are –110, –393, 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction :

$$N_2O_4(g) + 3CO(g) \longrightarrow N_2O(g) + 3CO_2(g)$$

Ans. *Refer Solved Example 27. (Page 29).*

Q. 13. Given

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \; ;$$

$$\Delta_r H^\circ = -92.4 \text{ kJ mol}^{-1}$$

What is the standard enthalpy of formation of NH_3 gas ?

Ans. *Refer Solved Example 23. (Page 28).*

Q. 14. Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data :

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);$$

$$\Delta_r H^\circ = -726 \text{ kJ mol}^{-1}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g);$$

$$\Delta_r H^\circ = -393 \text{ kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);$$

$$\Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$$

Ans. *Refer Solved Example 32. (Page 33).*

Q. 15. Calculate the enthalpy change for the process

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g)$$

and calculate bond enthalpy of C—Cl in $CCl_4(g)$.

$\Delta_{vap}H^\circ (CCl_4) = 30.5$ kJ mol^{-1}

$\Delta_f H^\circ (CCl_4) = -135.5$ kJ mol^{-1}

$\Delta_a H^\circ (C) = 715.0$ kJ mol^{-1},

where $\Delta_a H^\circ$ is enthalpy of atomisation

$\Delta_a H^\circ (Cl_2) = 242$ kJ mol^{-1}

Ans. *Refer Solved Example 50. (Page 47).*

Q. 16. For an isolated system, $\Delta U = 0$, what will be ΔS ?

Ans. Consider an isolated system such as two gases contained separately in two bulbs connected by a stopcock. The system is isolated from the surroundings so that $\Delta U = 0$. On opening the stopcock, the two gases mix up i.e., the system becomes more disordered. This means that $\Delta S > 0$.

Q. 17. For the reaction at 298 K,

$$2A + B \longrightarrow C$$

$\Delta H = 400$ kJ mol^{-1} and $\Delta S = 0.2$ kJ K^{-1} mol^{-1}

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range?

Ans. $\Delta G = \Delta H - T\Delta S = 0$

$$T = \frac{\Delta H}{\Delta S} = \frac{400 \text{ kJ mol}^{-1}}{0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}}$$

$$= 2000 \text{ K}$$

$\therefore$ For the reaction to be spontaneous i.e. for ΔG to be –ve, T should be greater than 2000 K

Q. 18. For the reaction

$$2Cl(g) \longrightarrow Cl_2(g)$$

What are the signs of ΔH and ΔS ?

Ans. The reaction involves the formation of bonds and hence energy is released i.e., ΔH = –ve

Since two particles give 1 particle, randomness decreases so that ΔS = –ve.

Q. 19. For the reaction

$$2A(g) + B(g) \longrightarrow 2D(g)$$

$\Delta U^\circ = -10.5$ kJ and $\Delta S = -44.1$ JK^{-1}

Calculate ΔG° for the reaction, and predict whether the reaction may occur spontaneously.

Ans. For the given reaction, $\Delta n_g = 2 - 3 = -1$

$\Delta H^\circ = \Delta U^\circ + \Delta n_g RT$

$= -10.5 \text{ kJ} + (-1) \times (8.314 \times 10^{-3} \text{ kJ}) \times (298 \text{ K})$

$= -10.5 - 2.48 = -12.98$ kJ

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$= -12.98 - 298 \; (-44.10 \times 10^{-3} \text{ kJ})$

$= -12.98 + 13.14 = 0.16$ kJ

Since ΔG° is +ve, the reaction is non-spontaneous.

Q. 20. The equilibrium constant for a reaction is 10. What will be the value of ΔG° ?

R = 8.314 JK^{-1} mol^{-1}, T = 300 K.

Ans. $\Delta G^\circ = -2.303 \; RT \log K$

$= -2.303 \times 8.314 \times 300 \log 10$

$= -5.744 \text{ kJ mol}^{-1}$.

Q. 21. Comment on the thermodyamic stability of $NO(g)$, given

$$(i) \; \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)$$

$$\Delta_r H^\circ = 90 \text{ kJ mol}^{-1}$$

$$(ii) \; NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g)$$

$$\Delta_r H^\circ = -74 \text{ kJ mol}^{-1}.$$

Ans. Since $\Delta_r H^\circ$ is +ve i.e., enthalpy of formation of NO is positive so $NO(g)$ is unstable. But $NO_2(g)$ is formed because energy is released.

Q. 22. Calculate the entropy change in surroundings when 1.00 mol of $H_2O(l)$ is formed under standard conditions, $\Delta_f H^\circ = -286$ kJ mol^{-1}.

Ans. *Refer Solved Example 52. (Page 59).*

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NCERT Exemplar Problems

Subjective Questions

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 119.*

Short Answer Questions *Carrying 2 or 3 marks*

Q.1. 18.0 g of water completely vapourises at 100° C and 1 bar pressure and the enthalpy change in the process is 40.79 kJ mol^{-1}. What will be the enthalpy change for vapourising two moles of water under the same conditions ? What is the standard enthalpy of vapourisation for water ?

Ans. 18.0 g of water = 1 mol

Standard enthalpy of vaporisation at 100° C and 1 bar pressure – 40.79 kJ mol^{-1}.

Enthalpy change in vaporisation of 2 mol of water = 2 × 40.79 = 81.58 kJ.

Q.2. One mole of acetone requires less heat to vaporise than 1 mol of water. Which of the two liquids has higher enthalpy of vaporisation ?

Ans. Water.

Q.3. Standard molar enthalpy of formation, $\Delta_f H°$ is just a special case of enthalpy of reaction, $\Delta_r H°$. Is the $\Delta_r H°$ for the following reaction same as $\Delta_f H°$? Give reason for your answer.

$CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$;

$\Delta_f H° = -178.3$ kJ mol^{-1}.

Ans. No, because $CaCO_3$ is formed from other compounds and not from its constituent elements.

Q.4. The value of $\Delta_f H°$ for NH_3 is –91.8 kJ mol^{-1}. Calculate enthalpy change for the following reaction :

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$$

Ans. Given

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g),$$

$$\Delta_f H° = -91.8 \text{ kJ mol}^{-1}$$

Multiplying by 2

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

$$\Delta H = -183.6 \text{ kJ}$$

or $$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$$

$$\Delta H = 183.6 \text{ kJ}.$$

Q.5. Enthalpy is an extensive property. In general, if enthalpy of an overall reaction A → B along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$ ..... represent enthalpies of intermediate reactions leading to product B. What will be the relation between $\Delta_r H$ for overall reaction and $\Delta_r H_1$, $\Delta_r H_2$ ..... etc. for intermediate reactions.

Ans. By Hess's law : $\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$ .....

Q.6. The enthalpy of atomisation for the reaction :

$$CH_4(g) \longrightarrow C(g) + 4H(g)$$

is 1665 kJ mol^{-1}. What is the bond enthalpy of C–H bond ?

Ans. Bond enthalpy of C–H bond = $\frac{1665}{4}$ = 416.25 kJ mol^{-1}.

Q.7. Use the following data to calculate $\Delta_{lattice} H°$ for NaBr.

$\Delta_{sub} H°$ for sodium metal = 108.4 kJ mol^{-1}
Ionization enthalpy of sodium = 496 kJ mol^{-1}
Electron gain enthalpy of bromine = –325 kJ mol^{-1}
Bond dissociation enthalpy of bromine = 192 kJ mol^{-1}
$\Delta_f H°$ for NaBr (s) = –360.1 kJ mol^{-1}

Ans. *Refer Text* (page 20), calculation of lattice enthalpy

$$\Delta_{lattice} H° = -735.5 \text{ kJ mol}^{-1}$$

Q.8. Given that $\Delta H = 0$ for mixing of two gases. Explain whether the diffusion of these gases into each other in a closed container is a spontaneous process or not ?

Ans. It is a spontaneous process. Although enthalpy change is zero but randomness or disorder (ΔS) increases and ΔS is positive. Therefore, in equation, $\Delta G = \Delta H - T\Delta S$, the term $T\Delta S$ will be negative. Hence ΔG will be negative.

Q.9. Heat has randomising influence on a system and temperature is the measure of average chaotic motion of particles in the system. Write the mathematical relation which relates these three parameters.

Ans. $\Delta S = \frac{q_{rev}}{T}$

Q.10. Increase in enthalpy of the surroundings is equal to decrease in enthalpy of the system. Will the temperature of system and surroundings be the same when they are in thermal equilibrium ?

Ans. Yes, when the system and the surroundings are in thermal equilibrium, their temperatures are same.

Q.11. At 298 K, K_p for the reaction : $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.98. Predict whether the reaction is spontaneous or not.

Ans.

$$\Delta_r G° = -RT \ln K_p$$

$$= -RT \ln(0.98) = -\text{ve}$$

Since $\Delta_r G°$ is negative, the reaction is spontaneous.

Q.12. A sample of 1.0 mol of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in Fig. 1. What will be the value of ΔH for the cycle as a whole ?

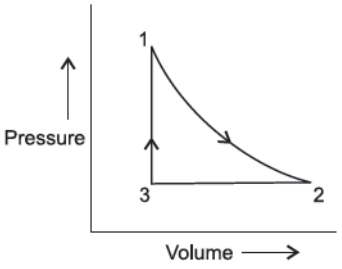

Fig. 1.

Ans. The net enthalpy change for the cyclic process is zero.

Q. 13. The standard molar entropy of $H_2O(l)$ is 70 JK^{-1} mol^{-1}. Will the standard molar entropy of $H_2O(s)$ be more or less than 70 JK^{-1} mol^{-1} ?

Ans. Less than 70 JK^{-1} mol^{-1}, because ice is more ordered than $H_2O(l)$.

Q. 14. Identify the state functions and path functions out of the following :

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enthalpy, entropy, heat, temperature, work, free energy.

Ans. **State functions :** enthalpy, entropy, temperature, free energy.
Path functions : heat, work.

Q.15. The molar enthalpy of vapourisation of acetone is less than that of water. Why ?

Ans. Molar enthalpy of vaporisation of acetone is less than that of water because of presence of hydrogen bonding in water.

Q.16. Which quantity out of $\Delta_r G$ or $\Delta_r G^\circ$ will be zero at equilibrium ?

Ans. $\Delta_r G$ will be zero.
$\Delta_r G^\circ$ will be zero for K = 1 because $\Delta G^\circ = -RT \ln K$
$\Delta_r G^\circ$ will be non-zero for other values of K.

Q.17. Predict the change in internal energy for an isolated system at constant volume.

Ans. For an isolated system, there is no transfer of energy as heat or as work so that $w = 0$ and $q = 0$
According to first law of thermodynamics :

$$\Delta U = q + w = 0 + 0 = 0$$

$$\therefore \quad \Delta U = 0$$

Q.18. Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions ? Explain.

Ans. The two conditions are :

(*i*) **Heat absorbed at constant pressure.**
According to first law of thermodynamics.

$$q = \Delta U + p\Delta V$$

At constant pressure, $q = q_p$

$$q_p = \Delta U + p\Delta V$$

But $\Delta U + p\Delta V = \Delta H$

$\therefore \quad q_p = \Delta H$ = change in enthalpy. Since ΔH is a state function, q_p is also a state function.

(*ii*) **Heat absorbed at constant volume.**

$$q = \Delta U + p\Delta V$$

At constant volume, $\Delta V = 0$

$$\therefore \quad q_v = \Delta U$$

Since ΔU is a state function, q_v is also a state function.

Q.19. Expansion of a gas in vacuum is called free expansion. Calculate the work done and the change in internal energy when 1 litre of ideal gas expands isothermally into vacuum until its total volume is 5 litre ?

Ans. During free expansion, external pressure is zero, so that
Work done, $w = -p_{ext}\Delta V$
$= -0(5 - 1) = 0$
Since the gas is expanding isothermally, $q = 0$

$$\Delta U = q + w$$
$$= 0 + 0 = 0$$

Q.20. Heat capacity (C_p) is an extensive property but specific heat (C) is an intensive property. What will be the relation between C_p and C for 1 mol of water ?

Ans. For water, molar heat capacity = 18 × Specific heat
or $C_p = 18 \times C$
But, specific heat,

$$C = 4.18\ Jg^{-1}\ K^{-1}$$

Heat capacity, $C_p = 18 \times 4.18\ JK^{-1}$
$= 75.3\ JK^{-1}$

Q.21. The difference between C_p and C_v can be derived using the empirical relation $H = U + pV$. Calculate the difference between C_p and C_v for 10 moles of an ideal gas.

Ans. $C_p - C_v = nR$
$= 10 \times 4.184\ J$
$= 41.84\ J$

Q.22. If the combustion of 1 g of graphite produces 20.7 kJ of heat, what will be molar enthalpy change ? Give the significance of sign also.

Ans. Molar enthalpy change of graphite = Enthalpy of combustion of 1 g × Molar mass
$= -20.7\ kJ\ g^{-1} \times 12\ g\ mol^{-1}$

$$\therefore \quad \Delta H = -2.48 \times 10^2\ kJ\ mol^{-1}$$

Since the value of ΔH is negative, the reaction is exothermic.

Q.23. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules minus amount of energy required to form all the bonds in the product molecules. What will be the enthalpy change for the following reaction.

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

Given that bond energy of H_2, Br_2, and HBr is 435 kJ mol^{-1}, 192 kJ mol^{-1} and 368 kJ mol^{-1} respectively.

Ans. $\Delta_r H^\circ = \Sigma$ B.E (reactants) – Σ B.E. (products)
$= $ B.E.(H_2) + B.E.(Br_2) – 2B.E.(HBr)
$= 435 + 192 - 2(368)$
$= -109\ kJ\ mol^{-1}$

Q.24. The enthalpy of vaporisation of CCl_4 is 30.5 kJ mol^{-1}. Calculate the heat required for the vapourisation of 284 g of CCl_4 at constant pressure. (Molar mass of CCl_4 = 154 u).

Ans. 1 mole of CCl_4 = 154 g
Enthalpy of vaporisation of 154 g of CCl_4
$= 30.5\ kJ$
Enthalpy of vaporisation of 284 g of

$$CCl_4 = \frac{30.5}{154} \times 284$$
$$= 56.25\ kJ$$

Q.25 What will be standard enthalpy of formation of $H_2O(l)$?

Ans. The required equation is :

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$$

The given equation is :

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta_r H^\circ = -572\ kJ\ mol^{-1}$$

Dividing the equation by 2,

or $$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$$

$$\Delta_f H^\circ(H_2O) = -\frac{572}{2}$$
$$= -286\ kJ\ mol^{-1}$$

Q.26. What will be the work done on an ideal gas enclosed in a cylinder, when it is compressed by a constant external pressure, p_{ext} in a single step as shown in Fig. 2. Explain graphically.

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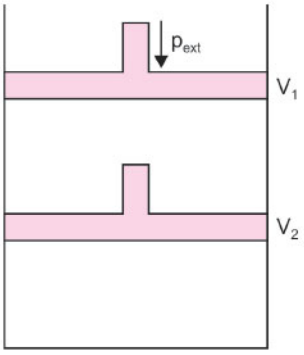

Fig. 2.

Ans. Work done on an ideal gas can be calculated from $p - V$ graph as shown in Fig. 3.

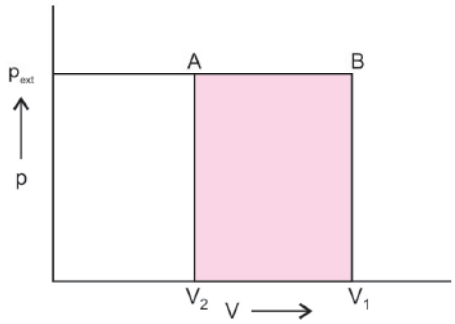

Fig. 3.

Work done is equal to shaded area AB V_1V_2

$$\text{Work done} = \text{Area}$$
$$= p_{ext}.(V_2 - V_1)$$
$$= p_{ext}\,\Delta V$$

Q.27. How will you calculate work done on an ideal gas in a compression, when change in pressure is carried out in infinite steps ?

Ans. Work done can be calculated with the help of $p - V$ plot. A $p - V$ plot of the work of compression is carried out by change in pressure in finite steps as shown below (Fig. 4).

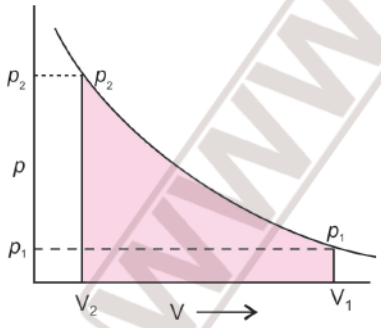

Fig. 4.

Work done is equal to the shaded area represented in the graph.

Q.28. Represent the potential energy/enthalpy change in the following processes graphically.

(*a*) Throwing a stone from the ground to roof.

(*b*) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons HCl(g)$ $\Delta_r H° = -92.32$ **kJ mol^{-1}**

In which of the processes potential energy/ enthalpy change is contributing factor to the spontaneity ?

Ans.

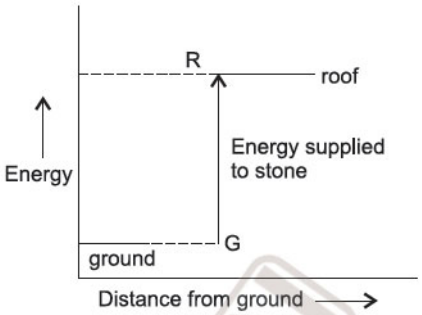

Fig. 5. (*a*)

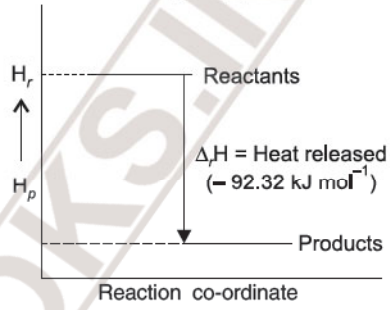

Fig. 5. (*b*)

In process (*b*), the enthalpy change is the contributing factor to the spontaneity.

Q.29. Enthalpy diagram for a particular reaction is given in Fig. 6. Is it possible to decide spontaneity of a reaction from given diagram. Explain.

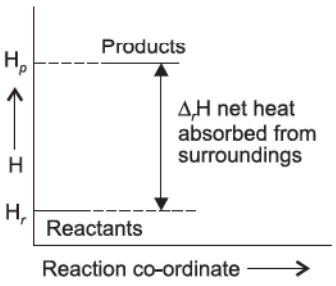

Fig. 6.

Ans. It is not possible to decide spontaneity of the reaction from the given diagram. Enthalpy change is one of the contributing factors in predicting the spontaneity of the reaction. But it is not the only factor. The another factor which helps to decide the spontaneity of a reaction is entropy factor. The resultant of these two factors known as Gibbs free energy is the main factor which decide the spontaneity of a reaction.

Q.30. 1.0 mol of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in Fig. 7. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K.

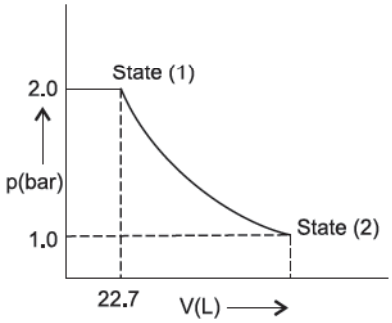

Fig. 7.

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Ans. It is clear from the figure that the process has been carried out in infinite steps and therefore, it is an isothermal reversible expansion process.

$$w = -2.303\ nRT\ \log\frac{V_2}{V_1}$$

But $p_1V_1 = p_2V_2$

or $\frac{V_2}{V_1} = \frac{p_1}{p_2} = \frac{2}{1} = 2$

or $w = -2.303\ nRT\ \log\frac{p_1}{p_2}$

$= -2.303 \times 1\ \text{mol} \times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1} \times 298\ \text{K} \times \log 2$

$= -5.706 \times 0.3010$

$= \mathbf{-1717.5\ J}$

Q.31. An ideal gas is allowed to expand against a constant presure of 2 bar from 10 L to 50 L in one step. Calculate the amount of work done by the gas. If the same expansion were carried out reversibly, will the work done be higher or lower than the earlier case ?

(Given that 1 L bar = 100 J)

Ans. $w = -p_{ext}\ (V_f - V_i)$

$= -2(50 - 10)$

$= -80$ L bar

$= -80 \times 100$ J or $= -8$ kJ

The negative sign shows that work is done by the system on the surroundings. Work done will be more in the reversible expansion because internal pressure and external pressure are almost same at every step.

Long Answer Questions *Carrying 5 marks*

Q.32. Derive the relationship between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.

Ans. *Refer Text (page 14).*

Q.33. Extensive properties depend on the quantity of matter but intensive properties do not. Explain whether the following properties are extensive or intensive.
Mass, internal energy, pressure, heat capacity, molar heat capacity, density, mole fraction, specific heat, temperature and molarity.

Ans. Extensive properties : Mass, internal energy, heat capacity.

Intensive properties : Pressure, molar heat capacity, density, mole fraction, specific heat, temperature and molarity.

Mole fraction and molarity of a solution are same whether we take a small amount of the solution or large amount of the solution. The ratio of two extensive properties is always intensive

$$\frac{\text{Extensive property}}{\text{Extensive property}} = \text{Intensive property}$$

e.g. $\text{Mole fraction} = \frac{\text{Moles (Extensive)}}{\text{Total no. of moles (Extensive)}}$

Q.34. The lattice enthalpy of an ionic compound is the enthalpy change for the dissociation of one mole of an ionic compound present into gaseous state, dissociates into its ions. It is impossible to determine it directly by experiment. Suggest and explain an indirect method to measure lattice enthalpy of NaCl(*s*).

Ans. Lattice enthalpy of an ionic compound can be determined indirectly by Born Haber cycle [*Refer Text (page 38-39)*].

Q.35. ΔG is net energy available to do useful work and is thus a measure of "free energy". Show mathematically that ΔG is a measure of free energy. Find the unit of ΔG. If a reaction has positive enthalpy change and positive entropy change, under what condition will the reaction be spontaneous ?

Ans. (*i*) *Refer Text (page 61-62).*

(*ii*) Since $-\Delta G = w_{useful}$, therefore, ΔG has the same units as those of work *i.e.* Joule.

(*iii*) $\Delta G = \Delta H - T\Delta S$. If ΔH = +ve, ΔS = +ve, then ΔG will be negative i.e. process will be spontaneous only when $T\Delta S > \Delta H$ in magnitude. This is possible when temperature T is high.

Q.36. Graphically show the total work done in a compression when the state of an ideal gas is changed reversibly and isothermally from (p_i, V_i) to (p_f, V_f). With the help of a *p*V plot compare the work done in the above case with that carried out against a constant external pressure p_f.

Ans.

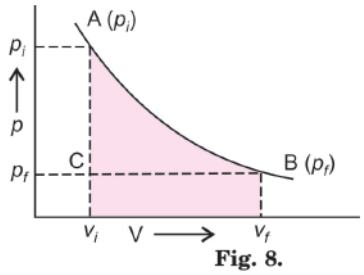

Fig. 8.

(*i*) Area AB V_iV_f represents total work done for reversible isothermal expansion from (p_i.V_i) to p_fV_f.

(*ii*) Area CB V_iV_f represents work done against constant pressure, p_f.

Work (*i*) is larger than work (*ii*).

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QUICK MEMORY TEST

A. Say True or False

1. The absolute value of internal energy of a substance can not be determined.
2. Enthalpy, entropy and free energy of formation of elementary substances in the standard state are taken as zero.
3. The energy of the universe remains constant whereas entropy of the universe is continuously increasing.
4. Heat and work are not state functions but their sum is a state function.
5. Diamond is more stable than graphite at room temperature and pressure.
6. Entropy of perfectly crystalline solid is taken as zero at 0 K.
7. At the melting point of ice, $\Delta G = 0$.
8. For $N_2(g)$ at 1 atm $\longrightarrow$ $N_2(g)$ at 0.5 atm, ΔS = –ve
9. An endothermic reaction which may be non spontaneous at low temperature because of entropy factor becomes spontaneous at high temperature.
10. The units of ΔG are same as those of energy.

B. Complete the missing links

1. During isothermal expansion of an ideal gas, the change in internal energy is .....
2. Bomb calorimeter is used to determine the value of ..... .
3. Standard state of carbon is .....
4. Heat of reaction at constant pressure is equal to ..... change.
5. In ..... process, no heat is exchanged between the system and the surroundings.
6. A stable compound has ..... enthalpy of formation.
7. In an isothermal process, ... remains constant.
8. For the process : normal egg. $\longrightarrow$ hard boiled egg, the sign of ΔS is .....
9. If ΔG is ..... the reaction does not proceed in the forward direction.
10. All combustion reactions are .....
11. The property of a system which does not depend upon the amount of substance is called ..... property.
12. A system which can exchange energy with the surroundings but not matter is called ..... system.
13. For triatomic gases such as CO_2, the ratio C_p/C_v is equal to .....
14. Molar heat capacity of iron (at. mass 56) will be ..... times its specific heat.
15. The allotropic form of sulphur for which standard enthalpy of formation is taken as zero is .....

C. Choose the correct alternative

1. Entropy and free energy of a system are ***extensive/intensive*** properties.
2. The total entropy change in a cyclic process is ***maximum/zero.***
3. The entropy of the universe is continuously ***decreasing/increasing.***
4. Zeroth law of thermodynamics forms the basis for the measurement of ***temperature/energy.***
5. The standard state of bromine is ***$Br_2(g)/Br_2(l)$.***
6. When a process is carried out in such a manner that the temperature remains constant, it is called ***isothermal/adiabatic.***

Answers QUICK MEMORY TEST

A. Say True or False

1. True
2. **False.** Enthalpy of formation and free energy of formation of elementary substances in the standard state are taken as zero but absolute entropy is not zero.
3. True
4. True
5. **False.** Graphite is more stable than diamond.
6. True
7. True
8. **False.** For the change ΔS = +ve.
9. True
10. True

B. Complete the missing links

1. zero
2. internal energy change (ΔU)
3. graphite
4. enthalpy
5. adiabatic
6. negative
7. temperature
8. negative
9. positive
10. exothermic
11. intensive
12. closed
13. 1.30
14. 56
15. rhombic sulphur.

C. Choose the correct alternative

1. extensive
2. zero
3. increasing
4. temperature
5. $Br_2(l)$
6. isothermal

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HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. A system is changed from an initial state to a final state by a process such that $\Delta H = q$. If the change from the initial state to the final state were measured by a different path, would ΔH and q be the same as that for the first path ?

Ans. ΔH is same because it is a state function.

q will be different for different paths.

Q.2. Predict the signs of ΔH and ΔS for the reaction:

$$2Cl(g) \longrightarrow Cl_2(g)$$

Ans. ΔH is –ve because bond energy is released.

ΔS is –ve because there is less randomness among the molecules than among the atoms.

Q. 3. Air contains about 99% of N_2 and O_2 gases. Why donot they combine to form NO under the standard conditions ? Standard Gibbs energy of formation of NO(g) is 86.7 kJ mol^{-1}.

Ans. For the combination of N_2 and O_2 to form NO, the standard Gibbs energy of formation,

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g) \text{ is +ve (+86.7 kJ mol}^{-1})$$

Therefore, this reaction is non-spontaneous under the standard conditions and hence N_2 and O_2 donot combine.

Q.4. Out of carbon (diamond) and carbon (graphite), whose enthalpy of formation is taken as zero and why ?

Ans. The enthalpy of formation of graphite is taken as zero because it is more commonly found in stable form of carbon.

Q.5. Is ΔH always greater than ΔU. Explain why or why not ?

Ans. ΔH is not always greater than ΔU because

$$\Delta H = \Delta U + \Delta n_g RT$$

Δn_g may be +ve or –ve

If $n_p - n_r$ = +ve

$$\Delta H = \Delta U + RT$$

$\therefore$ $\Delta H > \Delta U$

If $n_p - n_r$ = –ve

$$\Delta H = \Delta U - RT$$

$\therefore$ $\Delta H < \Delta U$

Q.6. Neither q nor w is a state function but $q + w$ is a state function. Explain why ?

Ans. Both q and w are not state functions but $q + w$ is equal to ΔU which is a state function.

Q.7. When is bond dissociation enthalpy equal to bond enthalpy ?

Ans. Bond dissociation enthalpy is equal to bond enthalpy for diatomic molecules such as H_2 (H–H), O_2 (O = O), etc. because only one bond is to be broken.

Q.8. At 1 atm will the $\Delta_f H°$ be zero for $Cl_2(g)$and $Br_2(g)$? Explain.

Ans. $\Delta_f H°$ for $Cl_2(g)$ will be zero but $\Delta_f H°$ for $Br_2(g)$ will not be zero because liquid bromine is its elementary state and not gaseous bromine.

Q.9. Under what conditions will a reaction be spontaneous if

(*i*) both ΔH and ΔS are positive

(*ii*) both ΔH and ΔS are negative ?

Ans. $\Delta G = \Delta H - T\Delta S$ and for a reaction to be spontaneous ΔG should be –ve.

(*i*) Both ΔH and ΔS are positive so that ΔG will be negative only if $T\Delta S > \Delta H$ in magnitude.

$$\Delta G = \Delta H - T\Delta S$$
$$= (+) - T(+)$$

Thus, either ΔS should be very large so that even if T is low, $T\Delta S$ is greater than ΔH, or if ΔS is small, T should be high so that $T\Delta S > \Delta H$.

(*ii*) If both ΔH and ΔS are negative, ΔG can be negative only if $T\Delta S < \Delta H$ in magnitude.

$$\Delta G = \Delta H - T\Delta S$$
$$= (-) - T(-)$$

This is possible only if either ΔH has large negative value or T is so low that $T\Delta S < \Delta H$.

Q.10. An exothermic reaction X → Y is spontaneous in the back direction. What is the sign of ΔS for the forward direction ?

Ans. The reaction is spontaneous in the backward direction, therefore, ΔG is positive in the foward direction. Now, forward reaction is exothermic, therefore, the entropy change for the forward direction should be negative and large ($T\Delta S > \Delta H$).

Q.11. Show that for an isothermal expansion of an ideal gas (*i*) $\Delta U = 0$ and (*ii*) $\Delta H = 0$.

Ans. (*i*) For one mole of an ideal gas, $C_v = \left(\frac{\Delta U}{\Delta T}\right)_v$.

or $\Delta U = C_v \Delta T$

For an isothermal process, T is constant so that

$$\Delta T = 0$$

$\therefore$ $\Delta U = 0$

(*ii*) $\Delta H = \Delta U + \Delta(PV)$

For an ideal gas, $PV = RT$

$\therefore$ $\Delta H = \Delta U + \Delta(RT)$

or $= \Delta U + R\Delta T$

Since T is constant

$$\Delta T = 0$$

$\therefore$ $\Delta H = 0$

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Q.12. While doing an experiment on bomb calorimeter, a student made the following statement :

$$\Delta H = \Delta U + p\Delta V.$$

Since in the experiment $\Delta V = 0$ hence $\Delta H = \Delta U$. Is the student right or wrong ? Justify.

Ans. The student is wrong because he has applied the equation $\Delta H = \Delta U + p\Delta V$, which holds good at constant pressure to a process which occurs at constant volume.

We know that,

$$H = U + pV$$

$$\therefore \quad \Delta H = \Delta U + \Delta(pV)$$

$$= \Delta U + p\Delta V + V\Delta p$$

For a process at constant pressure,

$$\therefore \quad \Delta H = \Delta U + p\Delta V$$

However, for a process at constant volume

$$\Delta V = 0$$

$$\therefore \quad \Delta H = \Delta U + V\Delta p$$

Q.13. Establish a relationship between ΔH and ΔU in Haber synthesis of ammonia assuming that gaseous reactants and products are ideal.

Ans. Haber synthesis for ammonia is :

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

$$\Delta n_g = 2 - (1 + 3) = -2$$

But $\quad \Delta H = \Delta U + \Delta n_g RT$

$$\therefore \quad \Delta H = \Delta U - 2RT$$

Q.14. How do the strengths of bonds in the reactants compare with those of their counterparts in the products for

(*i*) endothermic reaction ?

(*ii*) exothermic reaction ?

Ans. ΔH for a reaction involving bond enthalpies of products and reactants is

$$\Delta H = \Sigma \text{ Bond enthalpies of reactants} - \Sigma \text{ Bond enthalpies of products}$$

(*i*) For endothermic reaction, ΔH = +ve, which means that bond enthalpies of reactants are more than those of products. Hence, bonds in reactants are stronger than those in products.

(*ii*) For exothermic reaction, ΔH = –ve, which means that bond enthalpies of products are more than those of reactants. Hence, bonds in reactants are weaker than those of products or bonds in products are stronger than those of reactants. The stronger the bonds in products, the larger is the energy released.

Q.15. When an ideal gas expands in vacuum, there is neither absorption nor evolution of heat. Why ?

Ans. In an ideal gas, there are no intermolecular forces of attraction and therefore, no force opposes the expansion in vacuum. Hence, no energy is required to overcome these forces. Moreover, when a gas expands against vacuum, work done is zero because $p_{ext} = 0$. Therefore, internal energy of the system does not change, i.e. there is no absorption or evolution of heat.

Q.16. An average healthy man needs about 10000 kJ of energy per day. How much carbohydrates (in mass) he will have to consume assuming that all this energy needs are met only by carbohydrates in the form of glucose ? The enthalpy of combustion of glucose is 2816 kJ mol^{-1}.

Ans. Enthalpy of combustion of glucose = 2816 kJ mol^{-1}

Molecular mass of glucose ($C_6H_{12}O_6$) = $6 \times 12 + 12 \times 1 + 6 \times 16 = 180$

2816 kJ of energy evolved from glucose = 180 g

10000 kJ of energy evolved from glucose

$$= \frac{180}{2816} \times 10{,}000 = 63.9 \text{ g}$$

Q.17. Compute the heat of formation of liquid methyl alcohol in kilo joules per mole using the following data :

Heat of vaporisation of liquid methyl alcohol : 38 kJ/mol

Heat of formation of gaseous atoms from the elements in their standard states :

H = 218 kJ/mol,

C = 715 kJ/mol and O = 249 kJ/mol.

Average bond energies;

C — H = 415 kJ/mol, C–O = 356 kJ/mol and O–H = 463 kJ/mol

Ans. The required equation is

$$C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l)\ ;\ \Delta H = ?$$

Given equations are :

(*i*) $CH_3OH(l) \longrightarrow CH_3OH(g)$ $\quad \Delta H = 38$ kJ/mole

(*ii*) $C(s) \longrightarrow C(g)$ $\quad \Delta H = 715$ kJ/mole

(*iii*) $\frac{1}{2}H_2(g) \longrightarrow H(g)$ $\quad \Delta H = 218$ kJ/mole

(*iv*) $\frac{1}{2}O_2(g) \longrightarrow O(g)$ $\quad \Delta H = 249$ kJ/mole

The bond energies can be used to calculate,

$$CH_3OH(g) \longrightarrow C(g) + 4H(g) + O(g)$$

This involves breakage of three C—H bonds, one C—O bond and one O—H bond.

$\Delta H = (3 \times 415 + 356 + 463) = 2064$ kJ/mole.

(*v*) $CH_3OH(g) \longrightarrow C(g) + 4H(g) + O(g)$ $\quad \Delta H = 2064$ kJ/mole

The required equation can be obtained by carrying out the following operation :

(*ii*) + 4 × (*iii*) + (*iv*) – (*v*) – (*i*)

$\therefore \quad \Delta H = 715 + 4 \times 218 + 249 - 2064 - 38$

$= -266$ **kJ/mole.**

Q.18. The enthalpy change involved in the oxidation of glucose is – 2880 kJ mol^{-1}. 25% of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometre, what is the maximum distance that a person will be able to walk after eating 120 g of glucose ?

Ans. Mass of glucose = 120 g

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$$\text{Moles of glucose} = \frac{120}{180} = 0.67 \text{ mol}$$

Heat produced after eating 0.67 mol of glucose

$$= 0.67 \times 2880 = 1929.6 \text{ kJ}$$

Energy available for muscular work

$$= 1929.6 \times \frac{25}{100} = 482.5 \text{ kJ}$$

Maximum distance that the person will walk

$$= \frac{482.4}{100} = \mathbf{4.824\ km}.$$

Q.19. Determine the value of ΔH and ΔU for the reversible isothermal evaporation of 90.0 g of water at 100°C. Assume that water vapour behaves as an ideal gas and heat of evaporation of water is 540 cal g^{-1}. (R = 2.0 cal mol^{-1} K^{-1}).

Ans. $\Delta H = 90.0 \times 54.0 = 48600$ cal

$$\Delta H = \Delta U + p\Delta V$$

$$\text{where } p\Delta V = p(V_v - V_l)$$

Since volume of liquid is negligible in comparison to volume of vapour

$$\Delta H = \Delta U + p\Delta V$$

$$\Delta H = \Delta U + nRT$$

or $$\Delta U = \Delta H - nRT$$

$$= 48600 - \frac{90}{18} \times 2 \times 373 \qquad \left(n = \frac{90}{18}\right)$$

$$= 48600 - 3730$$

$$= \mathbf{44870\ cal.}$$

Q.20. The standard heat of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(g)$ are –76.2, –394.8 and –241.6 kJ mol^{-1} respectively. Calculate the amount of heat evolved by burning 1 m^3 of methane measured at N.T.P.

Ans. The burning of methane may be expressed as :

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

$$\Delta_f H^\circ = [\Delta_f H^\circ (CO_2) + 2\,\Delta_f H^\circ (H_2O)] - [\Delta_f H^\circ (CH_4) + 2\Delta_f H^\circ (O_2)]$$

$$= [-394.8 + 2 \times (-241.6)] - [-76.2 + 2 \times (0)]$$

$$= -801.8 \text{ kJ}$$

1 mole or 22.4 L of CH_4 evolve heat = 801.8 kJ

$$1\ m^3 \text{ or } 1000 \text{ L of } CH_4 \text{ evolve heat} = \frac{801.8 \times 1000}{22.4}$$

$$= \mathbf{35794.6\ kJ}$$

Q.21. Estimate the average S–F bond energy in SF_6. The values of standard enthalpy of formation of $SF_6(g)$, $S(g)$ and $F(g)$ are : –1100, 275 and 80 kJ mol^{-1} respectively.

Ans. The required equation is :

$$(i) \qquad SF_6(g) \longrightarrow S(g) + 6F(g) \qquad \Delta H = ?$$

Given equations are :

$$(ii) \quad S(s) + 3\,F_2(g) \longrightarrow SF_6(g) \qquad \Delta H = -1100 \text{ kJ mol}^{-1}$$

$$(iii) \quad S(s) \longrightarrow S(g) \qquad \Delta H = 275 \text{ kJ mol}^{-1}$$

$$(iv) \quad \frac{1}{2}F_2(g) \longrightarrow F(g) \qquad \Delta H = 80 \text{ kJ mol}^{-1}$$

To calculate ΔH for Eq (*i*), carry out the following :

$$(iii) + 6\,(iv) - (ii)$$

$$\therefore \Delta H = 275 + 6 \times 80 - (-1100)$$

$$= 1855 \text{ kJ mol}^{-1}$$

$$\therefore \text{S–F bond energy} = \frac{1855}{6} = 309.16 \text{ kJ mol}^{-1}$$

Q.22. At 0°C, ice and water are in equilibrium and ΔH = 6.0 kJ mol^{-1} for the process,

$$\mathbf{H_2O(s) \longrightarrow H_2O(l)}$$

What will be ΔS and ΔG for the conversion of ice into liquid water ?

Ans. For equilibrium reaction,

$$H_2O(s) \rightleftharpoons H_2O(l)$$

$$\Delta G = 0$$

$$\Delta G = \Delta H - T\Delta S$$

$$0 = \Delta H - T\Delta S$$

or $$\Delta S = \frac{\Delta H}{T} = \frac{6.00 \text{ kJ mol}^{-1}}{273}$$

$$= 0.0219 \text{ kJK}^{-1} \text{ mol}^{-1} = \mathbf{21.9\ JK^{-1}\ mol^{-1}}.$$

Q.23. 10 g of argon is compressed isothermally and reversibly at a temperature of 27°C from 10L to 5L. Calculate *q*, *w*, ΔU and ΔH for the process. R = 2.0 cal K^{-1} mol^{-1}, log 2 = 0.30, At. wt. of argon = 40.

Ans. $\text{Moles of argon} = \frac{10}{40}$

Work done for isothermal reversible process

$$w = -2.303\, nRT \log \frac{V_2}{V_1}$$

$$T = 273 + 27 = 300 \text{ K}, V_1 = 10\text{L}, V_2 = 5\text{L}, R = 2.0 \text{ cal}$$

$$\therefore \quad w = -2.303 \times \frac{10}{40} \times 2.0 \times 300 \log \frac{5}{10} = 103.991 \text{ cal}$$

For isothermal process,

$$\Delta U = 0$$

Now, $\Delta U = q + w$

$$0 = q + w \quad \text{or} \quad q = -w$$

$$\therefore \quad q = \mathbf{-103.991\ cal}$$

Q.24. Calculate the equilibrium constant for the following reaction at 298 K and 1 atm pressure :

$$\mathbf{NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)}$$

Given ΔH_f° at 298 K are : $NO(g)$ = 90.4 kJ mol^{-1} and $NO_2(g)$ = 33.8 kJ mol^{-1} ΔS° at 298 K for the reaction = – 70.0 JK^{-1} mol^{-1}, R = 8.31 JK^{-1} mol^{-1}.

Ans. Enthalpy change for the reaction,

$$\Delta H^\circ = \Sigma \Delta_f H^\circ \text{ (products)} - \Sigma \Delta_f H^\circ \text{ (reactants)}$$

$$= [\Delta_f H^\circ\, NO_2(g)] - [\Delta_f H^\circ\, NO(g) + \frac{1}{2}\Delta_f H^\circ\, O_2(g)]$$

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$$= [33.8] - [90.4 + \frac{1}{2} \times 0] = -56.6 \text{ kJ mol}^{-1}$$

$\Delta S^\circ = -70 \text{ JK}^{-1} \text{ mol}^{-1}$

Now $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, $T = 298$ K

$\therefore \Delta G^\circ = 56600 - 298 \times (-70) = -35740 \text{ J mol}^{-1}$

$$\log K = -\frac{\Delta G}{2.303\ RT}$$

or $$\log K = \frac{-35740}{2.303 \times 8.31 \times 298} = 6.267$$

$\therefore K = \text{Antilog } (6.267) = \mathbf{1.85 \times 10^6}$.

Q.25. 100mL of a liquid contained in an insulated container at a pressure of 1 bar. The pressure is steeply increased to 100 bar.

The volume of the liquid is decreased by 1 mL at this constant pressure. Find ΔH and ΔU.

Ans. $p_1 = 1$ bar, $p_2 = 100$ bar

$V_1 = 100$ mL $V_2 = 99$ mL

For adiabatic process, $q = 0$

$\Delta U = q + w$

$\Delta U = w$

$w = -p\Delta V$

$= -100\ (99 - 100) = 100$ bar mL

$\Delta H = \Delta U + \Delta pV$

$= 100 + p_2V_2 - p_1V_1$

$= 100 + (100 \times 99) - (1 \times 100)$

$= 100 + 9900 - 100 =$ **9900 bar mL.**

Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. Define ΔH. What will be the sign of ΔH in
   (*i*) exothermic reaction and
   (*ii*) endothermic reaction ?
2. What does the symbol ΔH denote? Define this quantity.
3. What is calorific value of a fuel?
4. What is the basic difference between the two notations $\Delta_r H$ and $\Delta_f H$?
5. How is enthalpy of sublimation related to enthalpy of fusion and enthalpy of vaporisation ?
6. What is enthalpy of combustion? Write chemical equation for the enthalpy of combustion of ethanol (C_2H_5OH).
7. The standard enthalpy of formation of sulphur dioxide (SO_2) is –296.9 kJ. Write thermochemical equation for this. What will be enthalpy of combustion of sulphur ?
8. Define enthalpy of fusion.
9. Define Hess's law of constant heat summation.
10. What is meant by bond dissociation enthalpy ?
11. Ammonia is prepared as
    $$3H_2(g) + N_2(g) \longrightarrow 2NH_3(g)$$
    What should be the sign of ΔS for this reaction ? Explain.
12. State first law of thermodynamics.
13. Why are we usually concerned with changes in enthalpy than changes in internal energy ?
14. Name the two criteria which must be met for a process to be spontaneous regardless of the temperature.
15. Give an example of a chemical reaction for which $\Delta H^\circ > \Delta U^\circ$.
16. Why do we feel cold on touching a block of ice ?
17. $\Delta_f H^\circ$ of Fe_2O_3 is –825 kJ. What is the enthalpy change for the reaction ?
    $$4Fe_2O_3 \longrightarrow 8Fe + 6O_2$$
18. The standard enthalpies of formation of three substances A, B and C are 201.6, – 52.6 and –106.4 kJ respectively. Arrange them in order of decreasing stability with respect to decomposition.
19. 100 ml of HCl solution and 100 ml of NaOH solution each having same molarity were mixed. 2.284 kJ of energy may be liberated during mixing.Calculate the molarity of each solution.
20. Define molar heat capacity and specific heat capacity.
21. What are the units of entropy and free energy ?
22. Explain the state of a reaction when $\Delta G = 0$.
23. Write Gibbs Helmholtz equation giving meanings of the symbols used.
24. What is the sign of ΔH for
    (*i*) evaporation of liquid water ?
    (*ii*) freezing of liquid water to ice ?
25. When an ideal gas expands in vacuum, there is neither absorption nor evolution of heat. Explain.
26. In a process, a system does 145 J of work on its surroundings while 85 J of heat is added to the system. What is ΔU for the system ?
27. How is free energy change related to equilibrium constant for the reaction ?
28. Predict ΔS for the reaction :
    $$NH_3\ (g) + HCl\ (g) \longrightarrow NH_4Cl\ (s)$$
29. Why does the entropy of a solid increase on melting ?
30. What is the effect of temperature on entropy ?
31. State the second law of thermodynamics.
32. Write mathematical statement of first law of thermodynamics.

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33. Predict the sign of ΔS for the reaction :

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

34. Predict whether the entropy of system increases or decreases during the oxidation of nitrogen :

$$N(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

35. Explain how an endothermic reaction can be spontaneous.

36. Which of the following will have larger entropy: a mole of ice at 0°C or a mole of water at the same temperature ?

37. What is entropy ? Give its units.

Short Answer Questions *Carrying 2 or 3 marks*

1. Is it possible for any process to have $\Delta H = \Delta E$? If yes, state under what conditions ? If no, state why not ?

2. State Hess's law and explain its one use.

3. Define the terms internal energy change and enthalpy change. How are they related ?

4. Explain heat and work as the modes of transference of energy between the system and the surroundings.

5. Define the terms :
(*i*) Enthalpy of formation (*ii*) Enthalpy of combustion.

6. What is a thermochemical equation ? Explain why is it essential to mention the physical states of reactants and products in thermochemical equations.

7. Define heat capacity, specific heat capacity and molar heat capacity. How are they related ?

8. Define the terms :
(*i*) Enthalpy of fusion (*ii*) Enthalpy of sublimation
(*iii*) Enthalpy of vaporisation.
How are these terms related ?

9. Differentiate between
(*i*) a change of state and a phase change
(*ii*) molar heat capacity and molar solution

N.C.E.R.T.

10. In what ways internal energy is different from enthalpy ? Explain both the terms with suitable examples.

11. What is the basic difference between enthalpy of formation and enthalpy of a reaction ? Illustrate with suitable examples.

12. Which of the following are state functions ?
(*i*) height of a hill
(*ii*) distance travelled in climbing the hill
(*iii*) energy change in climbing the hill.

13. Fill in the blanks :
(*a*) $C(s)\,(\text{graphite}) \longrightarrow C(g)$; $\Delta_r H^\circ = 716.7$ kJ
$\Delta_r H^\circ$ is the heat of ..... of graphite.
(*b*) $H_2O(l) \longrightarrow H_2O(s)$; $\Delta_r H^\circ = -6.01$ kJ
ΔH is the heat of ..... of water.
(*c*) $H_2O(l) \longrightarrow H_2O(g)$; $\Delta H = 40.7$ kJ
$\Delta_r H^\circ$ is the heat of ..... of water.
(*d*) $C_2H_6 + 7/2O_2 \longrightarrow 2CO_2 + 3H_2O$;
$\Delta_r H^\circ = -1560$ kJ
$\Delta_r H^\circ$ is the heat of ..... of ethane.
(*e*) $1/2\,N_2 + 3/2\,H_2 \longrightarrow NH_3$; $\Delta_r H^\circ = -45.2$ kJ
$\Delta_r H^\circ$ is the heat of ..... of ammonia.

14. Explain the following terms :
(*i*) System, surroundings
(*ii*) State function
(*iii*) Heat capacity, molar heat capacity

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15. What is the meant by enthalpy of formation ? Write equations to express enthalpies of formation of
(*i*) Sulphur trioxide (*ii*) Water
(*iii*) Ethyl alcohol.

16. Derive relationship between ΔH and ΔU. Give example when
(*i*) $\Delta H < \Delta U$ (*ii*) $\Delta H = \Delta U$ (*iii*) $\Delta H > \Delta U$

17. Define heat of combustion of a fuel. What is its significance.

18. What is bond energy ? How are the bond energies related to change in enthalpy of a reaction ?

19. How does Hess's law help in calculating the enthalpy change for the conversion of diamond to graphite ?

20. Explain
(*i*) Reversible and irreversible process.
(*ii*) Isothermal and adiabatic process.

21. What are extensive and intensive properties ? Give two examples of each.

22. Explain under what conditions does the enthalpy change in a reaction become equal to change in internal energy ?

23. Define a system. What are the types of a system ?

24. Give the appropriate reasons for the following :
(*i*) It is necessary to define the standard state.
(*ii*) It is preferable to determine the change in enthalpy than change in internal energy.
(*iii*) It is necessary to specify the phases of the reactants and products in a thermochemical equation.

25. State and explain first law of thermodynamics. Give its mathematical form.

26. What is the difference between an open system and a closed system ?

27. Define enthalpy of combustion. How is it measured ?

28. How is energy exchanged between the system and the surroundings in the form of
(*i*) heat (*ii*) work ?

29. (*i*) Define C_p and C_v. How are these related for an ideal gas ?
(*ii*) Which of the two C_p or C_v is larger and why ?

30. Acetic acid and hydrochloric acid react with KOH solution. The enthalpy of neutralisation of acetic acid is -55.8 kJ mol^{-1} while that of hydrochloric acid is -57.1 kJ mol^{-1}. Can you think of how are these different?

31. Explain the differences between :
Adiabatic and isothermal process

32. Define the following terms :
(*i*) System
(*ii*) Isothermal and adiabatic process
(*iii*) State variables/state functions
(*iv*) Work.

33. State whether each of the following processes will increase or decrease total energy content of the system :
(*a*) Heat transferred to the surroundings
(*b*) Work done by the system
(*c*) Work done on the system

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34. What do you mean by a spontaneous process ? Explain your answer with suitable examples. ***N.C.E.R.T.***

35. Explain the terms 'entropy', 'enthalpy' and 'free energy'.

36. Account for the fact that entropy of ice is less than that of water.

37. Why would you expect a decrease in entropy as a gas condenses into liquid ? Compare it with entropy decrease when a liquid sample is converted into solid. ***N.C.E.R.T.***

38. Correlate entropy and disorder with the help of fusion and vaporisation processes.

39. Explain the state of chemical reactions when :
(*i*) $\Delta G = 0$ (*ii*) $\Delta G < 0$ and (*iii*) $\Delta G > 0$

40. What is entropy change ? What is the change of entropy with change of (*i*) temperature and (*ii*) pressure ? Correlate the behaviour with the randomness.

41. Can ΔH be used as a sole criterion for the feasibility of a chemical reaction ? Explain with examples.

42. Fill in the blanks :
(*i*) The reaction which has a natural urge to proceed of its own is called ..... reaction.
(*ii*) In the freezing of water to ice enthalpy .....
(*iii*) The decrease in ..... is equal to the useful work done by the system.
(*iv*) If ΔG is ..... the reaction does not occur in the forward direction.

43. Define free energy and entropy of a system.

44. Predict whether the entropy increases or decreases for the following :
(*i*) 1 mol of liquid water changes to vapours.
(*ii*) 1 mol of chlorine is liquefied.

45. Define entropy and free energy of a system. Predict the feasibility of a reaction when :
(*i*) Both ΔH and ΔS increase.
(*ii*) Both ΔH and ΔS decrease.
(*iii*) ΔH decreases but ΔS increases.

46. For a reaction both ΔH and ΔS are positive. Under what conditions does the reaction occur spontaneously ?

47. Explain the physical significance of entropy.

48. Predict the sign of ΔS (positive or negative) for the following changes :
(*i*) $HCOOH(l) \longrightarrow H_2O(l) + CO_2(g)$
(*ii*) $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$
(*iii*) $I_2(s) \longrightarrow I_2(g)$
(*iv*) $2O_3(g) \longrightarrow 3O_2(g)$
(*v*) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

49. State giving reasons whether the entropy change for vaporisation of one mole of water will be more or less than entropy change per mole for fusion of ice.

50. What is entropy change ? Predict the sign of entropy change in each of the following giving reasons for your predictions :
(*i*) H_2 (at 25°C, 1 atm) $\longrightarrow$ H_2 (at 25°C and 10 atm)
(*ii*) H_2O (at 25°C, 1 atm) $\longrightarrow$ H_2O (at 50°C and 1 atm)
(*iii*) $2NH_4NO_3(s) \longrightarrow 2N_2(g) + 4H_2O(g) + O_2(g)$

51. (*a*) What is the value of free energy change for a reaction in equilibrium state ?
(*b*) How is free energy change related to equilibrium constant of the reaction ?

52. Comment on the statement that the energy of the universe remains constant but entropy of universe is always increasing.

53. Why is it that most of the reactions which are spontaneous at room temperature are exothermic, while the endothermic reactions are favoured only at very high temperatures ?

54. What is meant by free energy of a system ? How is it related to enthalpy and entropy of the system ? How is it useful for predicting the feasibility of a process ?

55. State and explain Gibbs Helmholtz equation.

56. Predict whether the following changes involve an increase or decrease of entropy :
(*a*) $Br_2(g) \longrightarrow 2Br(g)$
(*b*) $H_2O(l) \longrightarrow H_2O(s)$
(*c*) $Cr^{3+}(aq) + 6H_2O(l) \longrightarrow [Cr(H_2O)_6]^{3+}(aq)$
(*d*) Crystallisation of salt from brine solution
(*e*) $NaCl(s) \xrightarrow{\text{Water}} NaCl(aq)$
(*f*) Sublimation of ammonium chloride
(*g*) $CO_2 + H_2O \longrightarrow \underset{\text{Photo-synthesis}}{\overset{\text{light}}{\longrightarrow}}$ Carbohydrates $+ O_2$
(*h*) Naphthalene dissolving in benzene
(*i*) $CaCO_3(s) \longrightarrow CaO(s) + O_2(g)$

57. Predict the enthalpy change, free energy change and entropy change when ammonium chloride is dissolved in water and the solution becomes colder.

58. Define the terms :
(*i*) Free energy
(*ii*) Thermodynamic equilibrium
(*iii*) Entropy

59. Neither the enthalpy change nor the entropy change alone can be used to explain the spontaneity of a reaction. Explain.

60. Predict the sign of ΔG for a reaction that is
(*a*) Exothermic and accompanied by an increase in entropy.
(*b*) Endothermic and accompanied by increase in entropy.
(*c*) Can a temperature change affect the sign of ΔG in (*a*) or (*b*) ? If so, how ?

61. What is Gibbs free energy change ? Discuss its physical significance.

62. Explain the following :
(*a*) The entropy of a substance increases on going from the liquid to the vapour state at any temperature.
(*b*) Reactions with $\Delta_r G^\circ < 0$ always have an equilibrium constant greater than 1.
(c) An exothermic reaction is always thermodynamically spontaneous. ***N.C.E.R.T.***

63. How will you distinguish between the two ?
(*i*) Open and closed system.
(*ii*) Extensive and intensive properties.

64. What are spontaneous and non-spontaneous process ? Under what coditions will the reaction occur if :
(*i*) both ΔH and ΔS are positive
(*ii*) both ΔH and ΔS are negative ?

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65. What is free energy ? How is it related to the spontaneity of a reaction.

66. Taking a specific example show that ΔS_{total} is the criterion for spontaneity of a change.

Long Answer Questions *Carrying 5 marks*

1. Explain the following terms :
(*i*) First law of thermodynamics
(*ii*) Standard enthalpy of formation
(*iii*) Reversible and irreversible process
(*iv*) Isothermal and adiabatic process
(*v*) Bond enthalpy. ***N.C.E.R.T.***

2. State and explain Hess's law of constant heat summation. Discuss its important applications.

3. What are internal energy change and enthalpy change ? How are these related? Under what conditions both become equal ?

4. Explain the following terms :
(*i*) Enthalpy of formation
(*ii*) Enthalpy of combustion
(*iii*) Enthalpy of phase transition.

5. Write short notes on :
(*i*) Measurement of enthalpy of reaction.
(*ii*) Hess's law and its applications.

6. Differentiate between spontaneous and non-spontaneous processes by giving examples. Discuss the criterion for the spontaneity of a process.

7. Explain the following terms giving examples :
(*i*) System (*ii*) Surroundings
(*iii*) Entropy (*iv*) Enthalpy
(*v*) Free energy.

8. Explain free energy. Discuss the effect of temperature on free energy.

9. How is ΔG related to ΔH and $T\Delta S$? What is the meaning of $\Delta G = 0$?

10. (*a*) Explain the terms entropy and free energy. Why does entropy of a solid increase on fusion?
(*b*) What are spontaneous and non-spontaneous processes ? Explain that Gibbs free energy is a measure of useful work.

11. ΔG is net energy available to do useful work and is thus a measure of "free energy". Show mathematically that ΔG is a measure of free energy. Find the unit of ΔG. If a reaction has positive enthalpy change and positive entropy change, under what condition will the reaction be spontaneous ?

12. Graphically show the total work done in a compression when the state of an ideal gas is changed reversibly and isothermally from (p_i, V_i) to (p_f, V_f). With the help of a pV plot compare the work done in the above case with that carried out against a constant external pressure p_f.

Numerical Problems *carrying 5 marks*

1. The reaction between gaseous hydrogen and chlorine is

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$
$$\Delta_r H^\circ = -184.0 \text{ kJ}$$

(*i*) What is the enthalpy of formation of HCl ?
(*ii*) How much heat will be liberated at 298 K and 1 atm for the formation of 365 g of HCl ?

2. The enthalpies of combustion of $C_2H_2(g)$ and $C_2H_6(g)$ are -1301 kJ and -1561.5 kJ respectively. The enthalpy of formation of liquid water is -286 kJ. Calculate the enthalpy change for the reaction :

$$C_2H_2(g) + 2H_2(g) \longrightarrow C_2H_6(g)$$

3. The enthalpy of formation of carbon monoxide and steam are -110.5 and -243.0 kJ respectively. Calculate the heat of the reaction when steam is passed over coke as :

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$

4. Calculate the enthalpy of combustion of glucose from the following data :

$$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$$
$$\Delta_r H^\circ = -395.0 \text{ kJ}$$
$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$$
$$\Delta_r H^\circ = -269.4 \text{ kJ}$$
$$6C(\text{graphite}) + 6H_2(g) + 3O_2(g) \longrightarrow C_6H_{12}O_6(s)$$
$$\Delta_r H^\circ = -1169.9 \text{ kJ}$$

5. The heat evolved in the combustion of methane is given as :

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$
$$\Delta_r H^\circ = 890.3 \text{ kJ}$$

Calculate :
(*a*) how many grams of methane would be required to produce 445.15 kJ of heat on combustion ?
(*b*) how many grams of CO_2 would be formed when 445.15 kJ heat is evolved ?
(*c*) what volume of O_2 at S.T.P. would be used in the above combustion process ?

6. A gas mixture of 3.67 L of ethylene and methane on complete combustion at 25°C produce 6.11 L of CO_2. Find out the amount of heat evolved on burning 1 L of gas mixture. $\Delta_r H^\circ$ combustion of C_2H_4 and CH_4 are -1423 and -891 kJ mol^{-1} respectively.

7. Calculate the enthalpy of formation of HI (*g*) from the following data :

(*i*) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$
$\therefore \Delta_r H^\circ = -184.6$ kJ

(*ii*) $HCl(g) + aq \longrightarrow HCl(aq)$
$\Delta_r H^\circ = -72.43$ kJ

(*iii*) $HI(g) + aq \longrightarrow HI(aq)$
$\Delta_r H^\circ = -80.37$ kJ

(*iv*) $KOH(aq) + HCl(aq) \longrightarrow KCl(aq)$
$\Delta_r H^\circ = -57.49$ kJ

(*v*) $KOH(aq) + HI(aq) \longrightarrow KI(aq)$
$\Delta_r H^\circ = -57.19$ kJ

(*vi*) $Cl_2(g) + 2KI\ (aq) \longrightarrow 2KCl(aq) + I_2(s)$
$\Delta_r H^\circ = -219.4$ kJ

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8. Standard enthalpy of vaporization of benzene at its boiling point is 30.8 kJ mol^{-1}. For how long would a 100 W electric heater have to operate in order to vaporize a 100 g sample of benzene at its boiling temperature (power $= \frac{\text{energy}}{\text{time}} = 1\ W = 1\ J\ s^{-1}$)

9. When 1.3 g of butane C_4H_{10} was burnt in oxygen in a flame calorimeter containing 1.8 kg of water, the temperature rose from 25.3 to 33.3 °C. Calculate the enthalpy change for the combustion of 1 mol of butane ?

10. 0.562 g of graphite kept in a bomb calorimeter in excess of oxygen of 298 K and 1 atmospheric pressure was burnt according to the reaction :

$$C\ (\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$$

During the reaction, temperature rises from 298 K to 298.89 K. If the heat capacity of the calorimeter and its contents is 20.7 kJ K^{-1}, what is the enthalpy change for the above reaction at 298 K and 1 atm. ?

Hints & Answers for Revision Exercises

Very Short Answer Questions

1. (*i*) – ve (*ii*) + ve

5. $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$

6. $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

7. –296.9 kJ

11. ΔS = –ve

15. For the reaction :

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, $\Delta n_g = 2 - 1 = 1$

$\therefore \quad \Delta H = \Delta U + (1)\ RT \qquad \therefore \quad \Delta H > \Delta U$

16. Heat goes from our fingers to ice and we feel cold.

17. 3300 kJ

18. C > B > A

19. 0.4 M

21. $JK^{-1}\ mol^{-1}$, kJ mol^{-1}

22. Equilibrium state.

24. (*i*) ΔH = +ve (*ii*) ΔH = –ve

25. In ideal gases, there are no intermolecular forces and therefore, there is no expenditure of energy in overcoming these forces during expansion in vacuum.

26. $\Delta U = q + w = 85 + (-145) = -60$ J

27. $\Delta G^\circ = -2.303\ RT \log K$

28. decreases

29. increases because randomness increases

33. entropy ΔS is + ve

34. decreases

36. a mole of water has more entropy.

Short Answer Questions

13. (*a*) Sublimation (*b*) Fusion (*c*) Vaporisation (*d*) Combustion (*e*) Formation;

33. (*a*) decreases (*b*) decreases (*c*) increases.

39. (*i*) equilibrium

(*ii*) spontaneous in forward direction (*iii*) non-spontaneous in forward direction.

40. (*i*) The entropy increases with increase of temperature (randomness increases) and decreases with decrease in temperature (*ii*) For gases, entropy increases with decrease in pressure and decreases with increase in pressure. For liquids and solids, it remains practically independent of pressure.

42. (*i*) spontaneous (*ii*) decreases (*iii*) free energy (*iv*) positive

44. (*i*) increases (*ii*) decreases

45. (*i*) $T\Delta S > \Delta H$ (*ii*) $\Delta H > T\Delta S$ (*iii*) always spontaneous

46. Since both ΔH and $T\Delta S$ are positive, ΔG will be negative *i.e.*, reaction will be spontaneous ($\Delta G = \Delta H - T\Delta S$) only when $T\Delta S > \Delta H$.

48. (*i*) + ve (*ii*) –ve (*iii*) + ve (*iv*) + ve (*v*) – ve

49. $\Delta_{vap}S$ will be more than $\Delta_{fus}S$ because water vapours have more randomness than liquid water.

50. (*i*) ΔS = – ve

entropy decreases with increase in pressure.

(*ii*) ΔS = + ve

entropy increases with increase in temperature.

(*iii*) ΔS = + ve

gases are produced.

56. (*a*) increase (*b*) decrease (*c*) decrease (*d*) decrease (*e*) increase (*f*) increase (*g*) decrease (*h*) increase (*i*) increase.

60. (*a*) –ve

(*b*) Cannot be predicted because it depends upon the magnitude of ΔS, ΔH and T.

(*c*) A temperature change affects the sign in (*b*) by changing the magnitude of the temperature $-T\Delta S$

Numerical Problems

1. (*i*) Heat of formation of HCl is

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$$

$$\therefore \quad \Delta H = -\frac{184.0}{2} = \mathbf{-92.0\ kJ.}$$

(*ii*) For the formation of 1 mole HCl or 36.5 *g*, heat liberated = 92.0 kJ For the formation of 365 *g* of HCl, heat liberated

$$= \frac{92.0}{36.5} \times 365 = \mathbf{920\ kJ.}$$

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2. The given equations are

$$(i)\ C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$$
$$\Delta H = -1301 \text{ kJ}$$

$$(ii)\ C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$
$$\Delta H = -1561.5 \text{ kJ}$$

$$(iii)\ H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \Delta H = -286 \text{ kJ}$$

The required equation is

$$C_2H_2(g) + 2H_2(g) \longrightarrow C_2H_6(g) \qquad \Delta H = ?$$

$$(i)\ C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$$
$$\Delta H = -1301 \text{ kJ}$$

$$(iii) \times 2\ \ 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$
$$\Delta H = -572 \text{ kJ}$$

Add $(iv)\ C_2H_2(g) + 2H_2(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

$$\Delta H = -1873 \text{ kJ}$$

$$(ii)\quad C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$
$$\Delta H = -1561.5 \text{ kJ}$$

Subtract $C_2H_2(g) + 2H_2(g) \longrightarrow C_2H_6(g)$

$$\Delta H = -311.5 \text{ kJ}$$

3. We are given

$$(i)\ C(s) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \Delta H = -110.5 \text{ kJ}$$
$$(ii)\ H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \Delta H = -243.0 \text{ kJ}$$

Subtracting eq. (ii) from eq. (i), we get

$$C(s) + H_2O(g) \longrightarrow CO(g) + H(g)$$
$$\mathbf{\Delta H = +132.5 \text{ kJ}}$$

4. The given equations are :

$$(i)\ C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$$
$$\Delta H = -395.0 \text{ kJ}$$

$$(ii)\ H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$$
$$\Delta H = -269.4 \text{ kJ}$$

$$(iii)\ 6C(\text{graphite}) + 6H_2(g) + 3O_2(g) \longrightarrow C_6H_{12}O_6(s)$$
$$\Delta H = -1169.8 \text{ kJ}$$

The required equation is

$$(iv)\ C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

Multiply eq. (i) by 6 and subtract eq. (iii) from it.

$$(v)\ 6C(\text{graphite}) + 6O_2(g) \longrightarrow 6CO_2(g)$$
$$\Delta H = -2370 \text{ kJ}$$

$$(vi)\quad 6C(\text{graphite}) + 6H_2(g) + 3O_2(g) \longrightarrow C_6H_{12}O_6(s)$$
$$\Delta H = -1169.8 \text{ kJ}$$

Subtract

$$(vi)\ C_6H_{12}O_6(s) + 3O_2(g) \longrightarrow 6CO_2(g) + 6H_2(g)$$
$$\Delta H = -1200.2 \text{ kJ}$$

Multiply eq. (ii) by 6 and add to eq. (vi)

$$(vii)\ 6H_2(g) + 3O_2(g) \longrightarrow 6H_2O(l) \Delta H = -1616.4 \text{ kJ}$$

Adding $C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$

$$\mathbf{\Delta H = -2816.6 \text{ kJ}}$$

5. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 3H_2O(l)$

$$\Delta H = -890.3 \text{ kJ}$$

(a) According to the equation :

890.3 kJ of energy are produced from methane $= 16$ g

445.15 kJ of energy would be produced from

$$\text{methane} = \frac{16}{890.3} \times 445.15 = \mathbf{8} \text{ g}$$

(b) 890.3 kJ of heat is accompanied by the formation of $CO_2 = 44$ g 445.15 kJ of heat would be accompanied by the formation of $CO_2 = \frac{44}{890.3} \times 445.15 = \mathbf{22\ g}$

(c) 1 mole of O_2 at N.T.P. $= 22.4$ L

$\therefore$ 2 mole of O_2 at N.T.P. $= 44.8$ L

16 g of CH_4 required $O_2 = 44.8$ L

$$8\,g \text{ of } CH_4 \text{ would require } O_2 = \frac{42.8}{16} \times 8$$
$$= \mathbf{22.4\ L}$$

6. Combustion reactions of ethylene and ethane are :

$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O \quad \Delta H = -1423$ kJ

$CH_4 + O_2 \longrightarrow CO_2 + 2H_2O \quad \Delta H = -891$ kJ

Suppose the mixture contains $C_2H_4 = x$ litres

Volume of CH_4 in mixture $= (3.67 - x)$ litres

Now 1L of C_2H_4 gives $CO_2 = 2$L

x L of C_2H_4 will give $CO_2 = 2x$ L

1L of CH_4 gives $CO_2 = 1$L

$(3.67 - x)$ L of CH_4 gives $CO_2 = (3.67 - x)$L

Total CO_2 produced $= 2x + (3.67 - x) = (3.67 + x)$ L

Now $3.67 + x = 6.11$

or $x = 6.11 - 3.67 = 2.44$

Vol. of C_2H_4 in mixture $= 2.44$ L

Vol. of CH_4 in mixture $= 3.67 - 2.44 = 1.23$ L

Calculation of volume of gas in 1L mixture

$$\text{Vol. of } C_2H_4 \text{ in 1L mixture} = \frac{2.24}{3.67} = 0.6648 \text{ L}$$

$$\text{Vol. of } CH_4 \text{ in 1L mixture} = \frac{1.23}{3.67} = 0.3352 \text{ L}$$

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These volumes of gases are at 25°C. These are to be converted to 0°C (at N.T.P).

$$\text{Vol. of } C_2H_4 \text{ at } 0°C = \frac{0.6648 \times 298}{273} = 0.609 \text{ L}$$

$$\left(\text{Applying } \frac{V_1}{T_1} = \frac{V_2}{T_2}\right)$$

$$\text{Vol. of } CH_4 \text{ at } 0°C = \frac{0.3352 \times 298}{273} = 0.307 \text{ L}$$

Now 22.4 L of C_2H_4 (at N.T.P) give heat = 1423 kJ

$$0.609 \text{ L of } C_2H_4 \text{ will give heat} = \frac{1423}{22.4} \times 0.609$$

$$= 38.69 \text{ kJ}$$

Similarly, 22.4 L of CH_4 (at N.T.P) give heat = 891 kJ

$$0.307 \text{ L of } CH_4 \text{ (at N.T.P) will give heat} = \frac{891}{22.4} \times 0.307$$

$$= 12.21 \text{ kJ}$$

Total heat produced = 38.69 + 12.21 = **50.91 kJ**

7. The required equation is

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(s) \longrightarrow HI(g) \qquad \Delta H = ?$$

Divide eq. (*i*) by 2 and eq. (*vi*) by 2 and subtract

$$(i) \quad \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g) \qquad \Delta H° = -92.3 \text{ kJ}$$

$$(vi) \quad \frac{1}{2}Cl_2(g) + KI(g) \longrightarrow KCl(aq) + \frac{1}{2}I_2(s) \qquad \Delta H° = -109.7 \text{ kJ}$$

Subtract (*vii*)

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(s) + KCl(aq) \longrightarrow HCl(g) + KI(aq) \qquad \Delta H° = 17.4 \text{ kJ}$$

Add eq. (*iv*) to eq. (*vii*)

$$KOH(aq) + HCl(aq) \longrightarrow KCl(aq) \quad \Delta H° = -57.49 \text{ kJ}$$

Add

$$(viii) \quad \frac{1}{2}H_2(g) + \frac{1}{2}I_2(s) + KOH(aq) + HCl(aq) \longrightarrow HCl(g) + KI(aq) \quad \Delta H° = -40.09 \text{ kJ}$$

Subtract eq. (*v*) to eq. (*vii*)

$$KOH(aq) + HI(aq) \longrightarrow KI(aq) \quad \Delta H° = -57.19 \text{ kJ}$$

Subtract (*ix*)

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(s) + HCl(aq) \longrightarrow HCl(g) + HI(aq) \qquad \Delta H° = 17.10 \text{ kJ}$$

Add eq (*iv*) to eq. (*ix*)

$$HCl(g) + aq \longrightarrow HCl(aq) \qquad \Delta H° = -72.43 \text{ kJ}$$

Adding

$$(x) \quad \frac{1}{2}H_2(g) + \frac{1}{2}I_2(s) + aq \longrightarrow HI(aq) \qquad \Delta H° = -55.33 \text{ kJ}$$

Subtract eq. (*iii*) to eq. (*x*)

$$HI(g) + aq \longrightarrow HI(aq) \quad \Delta H° = -80.37 \text{ kJ}$$

Subtracting

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(s) \longrightarrow HI(g) \qquad \Delta H° = +25.04 \text{ kJ}$$

Thus, enthalpy of formation of HI (*g*) = **25.04 kJ**

8. Standard enthalpy of vaporization of benzene = 30.8 kJ mol^{-1}

Power of electric heater = 100 W = 100 J s^{-1}

Heat required to vaporize 100 g of

$$C_6H_6 = \frac{30.8 \times 10^3 \times 100}{78}$$

(Molar mass of benzene = 78) = 3 9.9 $\times 10^3$ J

100 watt = 100 Js^{-1}

100 J of heat is given in 1s

$$39.9 \times 10^3 \text{ J of heat is given in} = \frac{39900 \times 1}{100} = 399 \text{ s}$$

= 6.6 min

9. Increase in temperature of water = 33.3–25.3 = 8.0 K

Specific heat capacity of water = 4.18 J/K/g

Mass of water = 1.8 kg 1800 g

Amount of heat added to water by combustion of 1.3 g of butane,

$$q = m \times c \times \Delta T = 1800 \times 4.18 \times 8$$

$$= 60192 \text{ J}$$

Heat evolved in the combustion of 1 mol of butane,

$$= \frac{60192}{1.3} \times 58 = 2.685 \times 10^6 \text{ J}$$

$$= \mathbf{2.68 \times 10^3 \text{ kJ.}}$$

10. Quantity of heat absorbed by the calorimeter

$$q = C_v \times \Delta T$$

$$\Delta T = 298.89 - 298.0 = 0.89 \text{ K}$$

$$= -20.7 \text{ kJ/K} \times 0.89 \text{ K} = -18.4 \text{ kJ}$$

Enthalpy of combustion of 0.502 g of graphite

$$= -18.4 \text{ kJ}$$

Enthalpy of combustion of graphite for 1 mol

$$= -\frac{18.4}{0.502} \times 12.0 = -3.92 \times 10^2 \text{ kJ}$$

∴ Enthalpy of combustion of graphite

$$= \mathbf{3.92 \times 10^2 \text{ kJ.}}$$

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Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

Variation of heat of reaction with temperature (Kirchhoff's equation)

The heat of reaction varies with temperature. The variation of ΔH or ΔE with temperature is given by Kirchhoff's equation as :

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$$

where H_2 and H_1 are enthalpy changes at temperatures T_2 and T_1 respectively and ΔC_p is change in heat capacity at constant pressure. It is given as :

$\Delta C_p = \Sigma C_p$ of products $- \Sigma C_p$ of reactants.

Similarly, if E_2 and E_1 are internal energy changes at T_2 and T_1 respectively, then

$$\frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_v$$

ΔC_v is the change in heat capacities at constant volume, which is given as :

$\Delta C_v = \Sigma C_v$ of products $- \Sigma C_v$ of reactants.

ENERGY, HEAT AND WORK FOR SOME PROCESSES FOR IDEAL GASES

Isothermal Reversible Process

- Internal energy of an ideal gas depends upon temperature. Therefore,

$dU = 0$, $dH = d(U + pV) = dU + d(RT) = 0$ at constant T

$q = -w$

$$w = -nRT \ln \frac{V_2}{V_1} \text{ or } = -nRT \ln \frac{p_1}{p_2}$$

$$q = nRT \ln \frac{V_2}{V_1} \text{ or } = RT \ln \frac{p_1}{p_2}$$

Isothermal Isochoric Expansion

At constant T and p_{ext}

$$q = -w$$

$$= \int_{V_1}^{V_2} p_{ext}\, dV = p_{ext}\, \Delta V$$

i.e. all heat absorbed is used by the system in doing work and hence,

$$dU = 0$$

Also at constant, T, $d(pV) = d(nRT) = 0$

$$\therefore \quad dH = 0$$

Reversible Isothermal Expansion

For adiabatic process,

$q = 0$ or $dU = w$

$$\text{or } dV = \int_{T_1}^{T_2} C_v\, dT$$

$= C_v(T_2 - T_1)$ (if C_v is taken as constant).

The final temperature T_2, can be calculated from the relations,

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$p_1^{1-\gamma} T_1^{\gamma} = p_2^{1-\gamma} T_2^{\gamma}$$

$$\text{where } \gamma = \frac{C_p}{C_v}$$

OBJECTIVE TYPE QUESTIONS

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Select the Correct Answers :

Basic concepts of Thermodynamics, First Law and Heat Capacity

A1. For reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ which of the following is valid ?

(a) $\Delta H = \Delta U$ (b) $\Delta H > \Delta U$

(c) $\Delta H < \Delta U$ (d) None of the above.

A2. Which of the following represents the first law of thermodynamics ?

(a) $q = \Delta U - w$ (b) $\Delta H = q + w$

(c) $\Delta U = \Delta H + p\Delta V$ (d) $\Delta U = p\Delta V$.

A3. The volume of gas is reduced to half from its original volume. The specific heat will be

(a) reduce to half (b) be doubled

(c) remain constant (d) increase four times

A4. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.

(a) $q = 0, \Delta T \neq 0, w = 0$

(b) $q \neq 0, \Delta T = 0, w = 0$

(c) $q = 0, \Delta T = 0, w = 0$

(d) $q = 0, \Delta T < 0, w \neq 0$

Answers

A1. (c) **A2.** (a) **A3.** (c) **A4.** (c)

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A5. For an ideal gas, C_p and C_v are related as

(*a*) $C_p - C_v = R$ (*b*) $\frac{C_p}{C_v} = R$

(*c*) $C_p + C_v = R$ (*d*) $C_v - C_p = R$

A6. In an isothermal expansion of an ideal gas against vacuum, the work involved is :

(*a*) zero (*b*) maximum

(*c*) minimum (*d*) none of these.

A7. Which of the following statement is false ?

(*a*) work is a state function.

(*b* temperature is a state function.

(*c*) change in the state is completely defined when the initial and final states are specified.

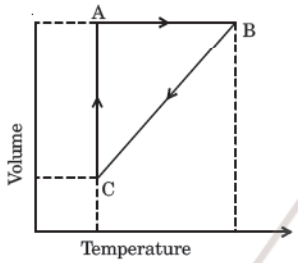
(*d*) work appears at the boundary of the system.

A8. In a closed insulator container, a liquid is stirred with a paddle to increases the temperature. Which of the following is true ?

(*a*) $\Delta U = w \neq 0, q = 0$ (*b*) $\Delta U = w = q \neq 0$

(*c*) $\Delta U = 0, w = q \neq 0$ (*d*) $w = 0, \Delta U = q \neq 0$

A9. Five moles of a gas is put through a series of changes as shown graphically in a cyclic process. The processes A ⟶ B, B ⟶ C and C ⟶ A respectively are :



(*a*) isochoric, isobaric, isothermal

(*b*) isobaric, isochoric, isothermal

(*c*) isothermal, isobaric, isochoric

(*d*) isochoric, isothermal, isobaric

(*e*) isobaric, isothermal, isochoric

(Kerala P.M.T. 2005)

A10. An ideal gas expands in volume from 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^5 Nm^{-2}. The work done is

(*a*) –900 J (*b*) –900 kJ

(*c*) 270 kJ (*d*) 900 kJ

(A.I.E.E.E. 2004)

Reaction Enthalpies and Bond Enthalpies

A11. The heat evolved in the combustion of benzene is given by the equation :

$C_6H_6(g) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$, $\Delta H = -3264.6$ kJ mol^{-1}

The heat energy change when 39 g of C_6H_6 are burnt in an open container will be :

(*a*) + 816.15 kJ mol^{-1} (*b*) + 1632.3 kJ mol^{-1}

(*c*) –1632.2 kJ mol^{-1} (*d*) –2448.45 kJ mol^{-1}

A12. Which of the following equations represents enthalpy of formation of H_2O ?

(*a*) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$; ΔH = –ve

(*b*) $2H_2O_2(g) \longrightarrow 2H_2O(l) + O_2(g)$; ΔH = + ve

(*c*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; ΔH = + ve

(*d*) $2H_2O(g) \longrightarrow 2H_2(g) + O_2(g)$; ΔH = + ve

A13. The enthalpy of neutralisation of NaOH with HCl is 57.1 kJ while with CH_3COOH, it is –55 kJ.

This happens because

(*a*) acetic acid is an organic acid

(*b*) acetic acid is little soluble in water

(*c*) acetic acid is a weak acid and requires lesser sodium hydroxide for neutralisation

(*d*) some heat is required to ionise acetic acid completely.

A14. The equations representing the combustion of carbon and carbon monoxide are :

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -394$ kJ/mol

$CO(s) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -284.5$ kJ/mol

the heat of formation of 1 mol of $CO(g)$ is :

(*a*) –109.5 kJ/mol (*b*) + 109.5 kJ/mol

(*c*) + 180.0 kJ/mol (*d*) + 100 kJ/mol.

A15. ΔH for the combustion of a compound is :

(*a*) positive

(*b*) zero

(*c*) negative

(*d*) may be positive or negative.

A16. Molar heat capacity of ethanol is 110.4 J K^{-1}. Its specific heat capacity is

(*a*) 2.4 (*b*) 55.2

(*c*) 5.078 (*d*) 110.4.

A17. Enthalpy of formation of ammonia is –46.0 kJ mol^{-1}. The enthalpy change for the reaction:

$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$

(*a*) 46.0 kJ mol^{-1} (*b*) –23.0 kJ mol^{-1}

(*c*) 92.0 kJ mol^{-1} (*d*) –92.0 kJ mol^{-1}.

A18. The $\Delta_f H^\circ$ for CO_2 (*g*), CO (*g*) and H_2O (*g*) are – 393.5, –110.5 and –241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction :

$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$ is

(*a*) 524.1 (*b*) 41.2

(*c*) –262.5 (*d*) –41.2

Answers

A5. (*a*) **A6.** (*a*) **A7.** (*a*) **A8.** (*a*) **A9.** (*a*) **A10.** (*a*) **A11.** (*c*) **A12.** (*c*) **A13.** (*d*) **A14.** (*a*) **A15.** (*c*) **A16.** (*a*) **A17.** (*c*) **A18.** (*b*)

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A19. Equal volumes of one molar HCl and H_2SO_4 are neutralised (separately) by dilute NaOH solution and x kcal and y kcal of heats are liberated. Which of the following is true ?

(a) $x = y$ (b) $x = 0.5\,y$

(c) $x = \frac{1}{2y}$ (d) None

A20. On the basis of thermochemical equations (*i*), (*ii*) and (*iii*), which of the algebric relationship is correct.

(*i*) $C\,(graphite) + O_2\,(g) \longrightarrow CO_2\,(g)$; $\Delta_r H = x$ kJ mol^{-1}

(*ii*) $C\,(graphite) + \frac{1}{2}O_2\,(g) \longrightarrow CO\,(g)$; $\Delta_r H = y$ kJ mol^{-1}

(*iii*) $CO\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow CO_2\,(g)$; $\Delta_r H = z$ kJ mol^{-1}

(a) $z = x + y$ (b) $x = y - z$

(c) $x = y + z$ (d) $y = 2z - x$

A21. During complete combustion of one mole of butane, 2658 kJ of heat is released. The thermochemical reaction for above change is

(a) $2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(l)$ $\Delta_c H = -2658.0$ kJ mol^{-1}

(b) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(g)$ $\Delta_c H = -1329.0$ kJ mol^{-1}

(c) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$ $\Delta_c H = -2658.0$ kJ mol^{-1}

(d) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$ $\Delta_c H = +2658.0$ kJ mol^{-1}

A22. The enthalpy of vaporisation of liquid water using data

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H = -285.77$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ $\Delta H = -241.84$ kJ is

(a) + 43.93 kJ mol^{-1} (b) – 43.93 kJ mol^{-1}

(c) + 527.61 kJ mol^{-1} (d) –527.61 kJ mol^{-1}.

A23. Given that

$C + O_2 \longrightarrow CO_2$ $\Delta H^\circ = -x$ kJ

$2CO + O_2 \longrightarrow 2CO_2$ $\Delta H^\circ = -y$ kJ

The enthalpy of formation of CO will be

(a) $y - 2x$ (b) $\frac{2x - y}{2}$

(c) $\frac{y - 2x}{2}$ (d) $2x - y$.

A24. Given : $C + 2S \longrightarrow CS_2$; $\Delta H = 117$ kJ

$C + O_2 \longrightarrow CO_2$; $\Delta H = -393$ kJ

$S + O_2 \longrightarrow SO_2$ $\Delta H = -297$ kJ

The heat of combustion of CS_2 to form CO_2 and SO_2 is

(a) –1104 kJ mol^{-1} (b) 1104 kJ mol^{-1}

(c) + 807 kJ mol^{-1} (d) – 807 kJ mol^{-1}

A25. When 5 g of sulphur is burnt to SO_2, 46 kJ of heat is liberated. What is the enthalpy of formation of sulphur dioxide ?

(a) – 147.2 kJ (b) + 147.2 kJ

(c) + 294.4 kJ (d) – 294.4 kJ.

A26. The enthalpy of formation of two compounds A and B are – 84 kJ and – 156 kJ respectively. Which one of the following statements is correct ?

(a) A and B are endothermic compounds

(b) A is more stable than B

(c) A is less stable than B

(d) Both are unstable.

A27. A cylinder of gas supplied by Bharat Petroleum is assumed to contain 14 kg of butane. If a normal family requires 20,000 kJ of energy per day for cooking, butane gas in the cylinder last for ..... days (ΔH_c of C_4H_{10} = – 2658 kJ per mole)

(a) 15 days (b) 20 days

(c) 50 days (d) 40 days

(e) 32 days *(Kerala P.M.T. 2004)*

A28. The enthalpy of hydrogenation of cyclohexene is –119.5 kJ mol^{-1}. If resonance energy of benzene is – 150.4 kJ mol^{-1}, its enthalpy of hydrogenation would be :

(a) – 208.1 kJ mol^{-1} (b) – 269.9 kJ mol^{-1}

(c) – 358.5 kJ mol^{-1} (d) – 508.9 kJ mol^{-1}

(C.B.S.E.Med. 2006)

A29. What would be the heat released when an aqueous solution containing 0.5 mol of HNO_3 is mixed with 0.3 mol of OH^- (enthalpy of neutralisation is –57.1 kJ)?

(a) 28.5 kJ (b) 17.1 kJ

(c) 45.7 kJ (d) 1.7 kJ

(e) 2.85 kJ *(Kerala C.E.T. 2005)*

Answers

A19. (b) **A20.** (c) **A21.** (c) **A22.** (a) **A23.** (c) **A24** (a) **A25.** (d) **A26.** (c) **A27.** (e) **A28.** (a) **A29.** (b)

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A30. If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and $\Delta_f H$ for the formation of XY is –200 kJmol^{-1}, the bond dissociation energy of X_2 will be

(*a*) 100 kJ mol^{-1} (*b*) 200 kJ mol^{-1}
(*c*) 800 kJ mol^{-1} (*d*) 400 kJ mol^{-1}

(*A.I.E.E.E. 2005*)

A31. The enthalpy change for the following processes are listed below :

$Cl_2(g) = 2Cl(g)$: 242.3 kJ mol^{-1}
$I_2(g) = 2I(g)$: 151.0 kJ mol^{-1}
$ICl(g) = I(g) + Cl(g)$: 211.3 kJ mol^{-1}
$I_2(s) = I_2(g)$: 62.76 kJ mol^{-1}

Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation for ICl (*g*) is

(*a*) – 16.8 kJ mol^{-1} (*b*) + 16.8 kJ mol^{-1}
(*c*) + 244.8 kJ mol^{-1} (*d*) – 14.6 kJ mol^{-1}

(*A.I.E.E.E. 2006*)

Entropy Change, Gibb's Energy and Spontaneity

A32. The entropy change can be calculated by using expression $\Delta S = \frac{q_{rev}}{T}$. When water freezes in a glass beaker, choose the correct statement amongst the following :

(*a*) ΔS (system) decreases but ΔS (surroundings) remains the same.
(*b*) ΔS (system) increases but ΔS (surroundings) decreases.
(*c*) ΔS (system) decreases but ΔS (surroundings) increases.
(*d*) ΔS (system) decreases and ΔS (surroundings) also decrease.

A33. For which of the following reactions, ΔS is not positive :

(*a*) $I_2(s) \longrightarrow I_2(g)$
(*b*) $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(l)$
(*c*) $2O_3(g) \longrightarrow 3O_2(g)$
(*d*) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

A34. If equilibrium constant for a reaction is K, then standard free energy change is :

(*a*) $\Delta G^\circ = -RT \log K$ (*b*) $\Delta G^\circ = RT \ln K$
(*c*) $\frac{\Delta G^\circ}{RT} = -\log K$ (*d*) $\frac{\Delta G^\circ}{RT} = -2.303 \log K$.

A35. For a reversible process at equilibrium, the change in entropy may be expressed as :

(*a*) $\Delta S = T\, q_{rev}$ (*b*) $\Delta S = \frac{\Delta H}{T}$
(*c*) $\Delta S = \frac{q_{rev}}{T}$ (*d*) $\Delta S = T\Delta H$.

A36. Free energy change is related to enthalpy and entropy changes as :

(*a*) $\Delta G = \Delta H - T\Delta S$ (*b*) $\Delta G = T\Delta S - \Delta H$
(*c*) $\Delta G^\circ = \frac{\Delta H - \Delta S}{T}$ (*d*) $\Delta G = \Delta H + T\Delta S$.

A37. For a spontaneous reaction, ΔG should be :

(*a*) positive
(*b*) negative
(*c*) equal to zero
(*d*) may be positive or negative.

A38. Which of the following conditions is not favourable for the feasibility of a reaction ?

(*a*) ΔH = + ve, TΔS = + ve and TΔS > ΔH
(*b*) ΔH = –ve, TΔS = + ve
(*c*) ΔH = –ve, TΔS = – ve and TΔS < ΔH
(*d*) ΔH = + ve, TΔS = + ve and TΔS < ΔH.

A39. The standard free energy change ΔG° is related to equilibrium constant K_p as

(*a*) $K_p = e^{-\Delta G^\circ/RT}$ (*b*) $K_p = \frac{-\Delta G^\circ}{RT}$
(*c*) $K_p = RT \ln \Delta G^\circ$ (*d*) $\Delta G = e^{-K_p/RT}$

A40. If $\Delta_f G^\circ$ for NH_3 (*g*) is –16.4 kJ mol^{-1}, then ΔG° for the reaction : $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ is

(*a*) 32.8 kJ mol^{-1}
(*b*) 16.4 kJ mol^{-1}
(*c*) – 16.4 kJ mol^{-1}
(*d*) – 32.8 kJ mol^{-1}

A41. An ideal gas is expanded adiabatically and irreversibly from volume V_i to V_f. Which of the following is correct?

(*a*) ΔS (sys) = +ve, ΔS (surr) = 0
(*b*) ΔS (sys) = 0, ΔS (surr) = +ve
(*c*) ΔS (sys) = 0, ΔS (surr) = 0
(*d*) ΔS (sys) = +ve, ΔS (surr) = –ve

A42. Which of the following is true for a reaction :

$H_2O(l) \rightleftharpoons H_2O(g)$ at 100°C, 1 atm pressure

(*a*) ΔH = ΔU (*b*) ΔU = 0
(*c*) ΔH = 0 (*d*) ΔH = TΔS

Answers

A30. (*c*) **A31.** (*b*) **A32.** (*c*) **A33.** (*b*) **A34.** (*d*) **A35.** (*c*) **A36.** (*a*) **A37.** (*b*) **A38.** (*d*) **A39.** (*a*) **A40.** (*d*) **A41.** (*b*) **A42.** (*d*)

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A43. Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is

(*a*) $\Delta S_{system} - \Delta S_{surrounding} > 0$
(*b*) $\Delta S_{system} > 0$
(*c*) $\Delta S_{surroundings} > 0$
(*d*) $\Delta S_{system} + \Delta S_{surrounding} > 0$

A44. A reaction occurs spontaneously if

(*a*) $T\Delta S < \Delta H$ and both ΔH and ΔS are +ve
(*b*) $T\Delta S > \Delta H$ and ΔH is +ve and ΔS is –ve
(*c*) $T\Delta S > \Delta H$ and both ΔH and ΔS are +ve
(*d*) $T\Delta S = \Delta H$ and both ΔH and ΔS are +ve

A45. The enthalpy and entropy change for the reaction :

$$Br_2(l) + Cl_2(g) \longrightarrow 2BrCl(g)$$

30 kJ mol^{-1} and 105 J K^{-1} mol^{-1} respectively. The temperature at which the reaction will be in equilibrium is :

(*a*) 273 K (*b*) 450 K
(*c*) 300 K (*d*) 285.7 K

A46. For a spontaneous reaction, the ΔG, equilibrium constant (K) and E°_{cell} will be respectively,

(*a*) – ve, > 1, + ve (*b*) +ve, > 1, – ve
(*c*) – ve, < 1, – ve (*d*) – ve, > 1, – ve

Answers

A43. (*d*) **A44.** (*c*) **A45.** (*d*) **A46.** (*a*)

B MULTIPLE CHOICE QUESTIONS *from Competitive Examinations*

AIPMT & Other State Boards' Medical Entrance

B1. Consider the following reactions :

(*i*) $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$
$\Delta H = -x_1$ kJ mol^{-1}

(*ii*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$
$\Delta H = -x_2$ kJ mol^{-1}

(*iii*) $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(l)$
$\Delta H = -x_3$ kJ mol^{-1}

(*iv*) $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$
$\Delta H = +x_4$ kJ mol^{-1}

Enthalpy of formation of $H_2O(l)$ is

(*a*) $+x_1$ kJ mol^{-1} (*b*) $-x_2$ kJ mol^{-1}
(*c*) $+x_3$ kJ mol^{-1} (*d*) $-x_4$ kJ mol^{-1}

(C.B.S.E. Med. 2007)

B2. Given that the bond energies of H—H and Cl—Cl are 430 kJ mol^{-1} and 240 kJ mol^{-1} respectively and $\Delta_f H$ for HCl is –90 kJ mol^{-1}, bond enthalpy of HCl is

(*a*) 245 kJ mol^{-1} (*b*) 290 kJ mol^{-1}
(*c*) 380 kJ mol^{-1} (*d*) 425 kJ mol^{-1}

(C.B.S.E. Med. 2007)

B3. If 150kJ of energy is needed for muscular work to walk a distance of 1km, then how much glucose one has to consume to walk a distance of 5km provided only 30% energy is available for muscular work. The enthalpy of combustion of glucose in 3000 kJ mol^{-1}.

(*a*) 75 g (*b*) 30 g
(*c*) 180 g (*d*) 150 g
(*e*) 45 g *(Kerala PMT 2007)*

B4. The average molar heat capacities of ice and water are respectively 37.8 J/mol and 75.6 J/mol and the enthalpy of fusion of ice is 6.012 kJ/mol. The amount of heat required to change 10 g of ice at –10°C to water at 10°C would be

(*a*) 2376 J (*b*) 4752 J
(*c*) 3970 J (*d*) 1128 J
(*e*) 1985 J *(Kerala PMT 2008)*

B5. Which of the following are not state functions?

(*i*) $q + w$ (*ii*) q (*iii*) w (*iv*) H – TS
(*a*) (*i*) and (*iv*) (*b*) (*ii*), (*iii*) and (*iv*)
(*c*) (*i*), (*ii*) and (*iii*) (*d*) (*ii*) and (*iii*)

(CBSE Med. 2008)

B6. Entropy changes for the process

$$H_2O(l) \longrightarrow H_2O(g)$$

at normal pressure and at 274 K are given below :

$\Delta S_{system} = -22.13$, $\Delta S_{surroundings} = +22.05$

The process is non-spontaneous because

(*a*) ΔS_{system} is –ve (*b*) $\Delta S_{surroundings}$ is +ve
(*c*) $\Delta S_{universe}$ is –ve (*d*) $\Delta S_{system} \neq \Delta S_{surroundings}$

(A.M.U. PMT 2009)

Answers

B1. (*b*) **B2.** (*d*) **B3.** (*d*) **B4.** (*c*) **B5.** (*d*) **B6.** (*c*)

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B7. The heats of atomisation of PH_3 (g) and $P_2H_4(g)$ are 954 kJ mol^{-1} and 1485 kJ mol^{-1} respectively. The P—P bond energy in kJ mol^{-1} is

(a) 213 (b) 426
(c) 318 (d) 1272
(e) 107 *(Kerala P.M.T. 2009)*

B8. The values of ΔH and ΔS for the reaction,

$$C(graphite) + CO_2(g) \longrightarrow 2CO(g)$$

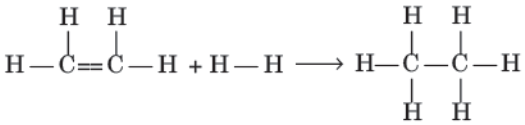
are 170 kJ and 170 J/K respectively. This reaction will be spontaneous at

(a) 910 K (b) 1110 K
(c) 510 K (d) 710 K
(C.B.S.E. PMT 2009)

B9. From the following bond energies :

H—H bond energy : 431.37 kJ mol^{-1}
C=C bond energy : 606.10 kJ mol^{-1}
C—C bond energy : 336.49 kJ mol^{-1}
C—H bond energy : 410.50 kJ mol^{-1}

Calculate the bond enthalpy of the following reaction :



(a) –243.6 kJ/mol (b) –120.0 kJ/mol
(c) 553.0 kJ/mol (d) 1523.6 kJ/mol
(C.B.S.E. PMT 2009)

B10. Standard entropies of X_2, Y_2 and XY_3 are 60, 40 and 50 kJ mol^{-1} respectively. For the reaction :

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3 \; ; \; \Delta H = -30 \text{ kJ}$$

to be at equilibrium, the temperature should be

(a) 500 K (b) 750 K
(c) 1000 K (d) 1250 K
(C.B.S.E. PMT 2010)

B11. Four grams of graphite is burnt in a bomb calorimeter of heat capacity of 30 kJ K^{-1} in excess of oxygen at 1 atmospheric pressure. The temperature rises from 300 to 304 K. What is the enthalpy of combustion of graphite (in kJ mol^{-1}) ?

(a) 360 (b) 1440
(c) –360 (d) –1440
(e) –520 *(Kerala PMT 2011)*

B12. Enthalpy change for the reaction,
$4H(g) \rightarrow 2H_2(g)$ is –869.6 kJ.
The dissociation energy of H – H bond is

(a) –434.8 kJ (b) –869.6 kJ
(c) + 434.8 kJ (d) +217.4 kJ
(AIPMT 2011)

B13. Which of the following is correct option for free expansion of an ideal gas under adiabatic condition ?

(a) $q = 0, \Delta T \neq 0, w = 0$ (b) $q \neq 0, \Delta T = 0, w = 0$
(c) $q = 0, \Delta T = 0, w = 0$ (d) $q = 0, \Delta T < 0, w \neq 0$
(AIPMT 2011)

B14. Choose the reaction with negative ΔS value.

(a) $2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$
(b) $Cl_2(g) \longrightarrow 2Cl(g)$
(c) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
(d) $2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$
(e) $H_2O(\ell) \longrightarrow H_2O(g)$ *(Kerala P.M.T. 2012)*

B15. Standard enthalpy of vaporisation $\Delta_{vap}H°$ for water at 100°C is 40.66 kJ mol^{-1}. The internal energy of vaporisation of water at 100°C (in kJ mol^{-1}) is

(a) + 37.56 (b) – 43.76
(c) + 43.76 (d) + 40.66
(Assume water vapour to behave like an ideal gas)
(A.I.P.M.T. 2012)

B15. In which of the following reactions, standard reaction entropy change ($\Delta S°$) is positive and standard Gibb's energy change ($\Delta G°$) decreases sharply with increasing temperature ?

(a) $C\text{ (graphite)} + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

(b) $CO\text{ (g)} + \frac{1}{2}O_2(g) \longrightarrow CO_2(s)$

(c) $Mg_{(s)} + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$

(d) $\frac{1}{2}C\text{ (graphite)} + \frac{1}{2}O_2(g) \longrightarrow \frac{1}{2}CO_2(g)$
(A.I.P.M.T. 2012)

B17. The enthalpy of fusion of water is 1.435 kcal/mol. The molar entropy change for the melting of ice at 0°C is

(a) 10.52 cal/(mol K) (b) 21.04 cal/(mol K)
(c) 5.260 cal/(mol K) (d) 0.526 cal/(mol K)
(A.I.P.M.T. 2012)

B18. In the following reaction:

$4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g)$; $\Delta H = -110$ kJ;

if $N_2O_5(s)$ is formed instead of $N_2O_5(g)$ in the reaction, the enthalpy change (in kJ) would be (enthalpy of sublimation of $N_2O_5(s)$ is + 53 kJ mol^{-1}).

(a) –216 (b) –162
(c) +108 (d) +216
(e) +162 *(Kerala PMT 2014)*

Answers

B7. (a) **B8.** (b) **B9.** (b) **B10.** (b) **B11.** (c) **B12.** (c) **B13.** (c) **B14.** (c) **B15.** (a) **B16.** (a)
B17. (a) **B18.** (a)

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B19. For the reaction, $X_2O_4(l) \longrightarrow 2XO_2(g)$
$\Delta U = 2.1$ kcal, $\Delta S = 20$ cal K^{-1} at 300 K
Hence, ΔG is
(a) 2.7 kcal (b) –2.7 kcal
(c) 9.3 kcal (d) –9.3 k cal *(AIPMT 2014)*

B20. The enthalpies of solution for copper sulphate pentahydrate and anhydrous copper sulphate are respectively 11.7 and –65.5 kJ mol^{-1}. The hydration enthalpy of anhydrous copper sulphate is
(a) 53.8 kJ mol^{-1} (b) –9.8 kJ mol^{-1}
(c) –77.2 kJ mol^{-1} (d) –53.8 kJ mol^{-1}
(e) 77.2 kJ mol^{-1} *(Kerala PMT 2015)*

B21. The standard enthalpy of formation of $NH_3(g)$ is –91.8 kJ mol^{-1}. The amount of heat required to decompose 34 g of $NH_3(g)$ into its elements is
(a) 183.6 kJ (b) 91.8 kJ
(c) 45.9 kJ (d) 137.7 kJ
(e) 275.4 kJ *(Kerala PMT 2015)*

B22. Calculate the work done by 16 g of oxygen gas (assume ideal behaviour) of molar mass 32 g mol^{-1} undergoing isothermal reversible expansion at 300 K from an initial volume of 2.5 L to the final volume of 25 L in litre atm.
($R = 8.2 \times 10^{-2}$ L atm K^{-1} mol^{-1})
(a) –56.64 (b) 28.32
(c) 113.28 (d) 56.64
(e) –113.28 *(Kerala PMT 2015)*

B23. The heat of combustion of carbon to CO_2 is –393.5 kJ/mol. The heat released for the formation of 35.2 g of CO_2 from carbon and oxygen gas is:
(a) –630 kJ (b) –3.26 kJ
(c) –315 kJ (d) + 315 kJ
(AIPMT 2015)

B24. Which of the following statements is correct for a reversible process in a state of equilibrium?
(a) $\Delta G^\circ = -2.30$ RT log K
(b) $\Delta G^\circ = 2.30$ RT log K
(c) $\Delta G = -2.30$ RT log K
(d) $\Delta G = 2.30$ RT log K *(AIPMT 2015)*

B25. The correct thermodynamic conditions for the spontaneous reaction at all temperatures is
(a) $\Delta H < 0$ and $\Delta S > 0$ (b) $\Delta H < 0$ and $\Delta S < 0$
(c) $\Delta H < 0$ and $\Delta S = 0$ (d) $\Delta H > 0$ and $\Delta S < 0$
(NEET 2016)

B26. For a sample of perfect gas when its pressure is changed isothermally from p_i to p_f, the entropy change is given by

(a) $\Delta S = nR\ ln\left(\frac{p_f}{p_i}\right)$ (b) $\Delta S = nR\ ln\left(\frac{p_i}{p_f}\right)$

(c) $\Delta S = nRT\ ln\left(\frac{p_f}{p_i}\right)$ (d) $\Delta S = RT\ ln\left(\frac{p_i}{p_f}\right)$

(NEET 2016)

B27. For a given reaction, $\Delta H = 35.5$ kJ mol^{-1} and $\Delta S = 83.6$ J K^{-1} mol^{-1}. The reaction is spontaneous at (assume that ΔH and ΔS do not vary with temperature.)
(a) $T > 425$ K (b) all temperatures
(c) $T > 298$ K (d) $T < 425$ K
(NEET 2017)

B28. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy ΔU of the gas in joules will be
(a) –500 J (b) –505 J
(c) +505 J (d) 1136.25 J
(NEET 2017)

B29. The bond dissociation energies of X_2, Y_2 and XY are in the ratio of 1 : 0.5 : 1. ΔH for the formation of XY is –200 kJ mol^{-1}. The bond dissociation energy of X_2 will be
(a) 200 kJ mol^{-1} (b) 100 kJ mol^{-1}
(c) 800 kJ mol^{-1} (d) 400 kJ mol^{-1}
(NEET 2018)

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B30. Assuming the water vapour is an ideal gas, the internal energy change (ΔU) when 1 mole of water is vapourised at 1 bar pressure and 100°C (given molar enthalpy of vapourisation of water at 1 bar and 373 K = 41 kJ mol^{-1} and R = 8.3 J mol^{-1} K^{-1}) will be
(a) 3.7904 kJ mol^{-1} (b) 37.904 kJ mol^{-1}
(c) 41.00 kJ mol^{-1} (d) 4.100 kJ mol^{-1}
(A.I.E.E.E. 2007)

B31. In conversion of limestone to lime,
$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$
the values of ΔH° and ΔS° are + 179.1 kJ mol^{-1} and 160.2 J/K respectively at 298 K and 1 bar. Assuming that ΔH° and ΔS° do not change with temperature, the temperature above which conversion of limestone to lime will be spontaneous is :
(a) 1200 K (b) 845 K
(c) 1118 K (d) 1008 K *(A.I.E.E.E. 2007)*

Answers

B19. (b) **B20.** (c) **B21.** (a) **B22.** (b) **B23.** (c) **B24.** (a) **B25.** (a) **B26.** (b) **B27.** (a) **B28.** (b)
B29. (c) **B30.** (b) **B31.** (c)

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B32. Using the following thermochemical equations
(*i*) $S(Rh) + 3/2\ O_2(g) \longrightarrow SO_3(g)$; $\Delta H = -2x$ kJ/mol
(*ii*) $SO_2(g) + 1/2\ O_2(g) \longrightarrow SO_3(g)$; $\Delta H = -y$ kJ/mol
Find out the heat of formation of $SO_2(g)$ in kJ/mol
(*a*) $(2x + y)$ (*b*) $(x + y)$
(*c*) $(2x/y)$ (*d*) $(y - 2x)$
(*e*) $(2x - y)$ *(Kerala PET 2008)*

B33. Oxidising power of chlorine in aqueous solution can be determined by parameters indicated below :

$$\frac{1}{2}Cl_2(g) \xrightarrow{1/2\Delta_{diss}H} Cl(g) \xrightarrow{\Delta_{eg}H} Cl^-(g) \xrightarrow{\Delta_{hyd}H} Cl^-(aq)$$

The energy involved in the conversion of $1/2Cl_2(g)$ to $Cl^-(aq)$ (using data, $\Delta_{diss}H_{Cl_2} = 240$ kJ mol^{-1}, $\Delta_{eg}HCl = -349$ kJ mol^{-1}, $\Delta_{hyd}H_{Cl^-} = -381$ kJ mol^{-1}) will be
(*a*) + 120 kJ mol^{-1} (*b*) +152 kJ mol^{-1}
(*c*) – 610 kJ mol^{-1} (*d*) – 850 kJ mol^{-1}
(A.I.E.E.E. 2008)

B34. In a fuel cell, methanol is used as fuel and oxygen is used as an oxidiser. The reaction is :

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

At 298 K, standard Gibb's energies of formation for $CH_3OH(l)$, $H_2O(l)$ and $CO_2(g)$ are –166.2, –237.2 and –394.4 kJ/mol respectively. If standard enthalpy of combustion of methanol is –726 kJ/mol, efficiency of the fuel cell will be :
(*a*) 80% (*b*) 87%
(*c*) 90% (*d*) 97%*(A.I.E.E.E. 2009)*

B35. On the basis of the following thermochemical data ($\Delta_f G^\circ\ H^+(aq) = 0$)

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq),\quad \Delta H = 57.32\ kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l),\quad \Delta H = -286.2\ kJ$$

The value of enthalpy of formation of OH^- at 25°C is
(*a*) –22.88 kJ (*b*) –228.88 kJ
(*c*) +228.88 kJ (*d*) –343.52 kJ
(A.I.E.E.E. 2009)

B36. The standard enthalpy of formation of NH_3 is – 46.0 kJ mol^{-1}. If the enthalpy of formation of H_2 from its atoms is – 436 kJ mol^{-1} and that of N_2 is – 712 kJ mol^{-1}, the average bond enthalpy of N – H bond in NH_3 is
(*a*) + 1056 kJ mol^{-1} (*b*) – 1102 kJ mol^{-1}
(*c*) – 964 kJ mol^{-1} (*d*) + 352 kJ mol^{-1}
(A.I.E.E.E. 2010)

B37. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both + ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when
(*a*) T_e is 5 times T (*b*) $T = T_e$
(*c*) $T_e > T$ (*d*) $T > T_e$ *(A.I.E.E.E. 2010)*

B38. One mole of an ideal gas expands at a constant temperature of 300 K from an initial volume of 10 litre to a final volume of 20 litre. The work done in expanding the gas is
(*a*) 750 Joule (*b*) 1728 Joule
(*c*) 1500 Joule (*d*) 3456 Joule
(AMU Engg. 2011)

B39. Molar heat capacity of aluminium is 25 JK^{-1} mol^{-1}. The heat necessary to raise the temperature of 54 g of aluminium (Atomic mass 27 g mol^{-1}) from 30° C to 50° C is
(*a*) 1.5 kJ (*b*) 0.5 kJ
(*c*) 1.0 kJ (*d*) 2.5 kJ
(*e*) 2.0 kJ *(Kerala PET 2011)*

B40. The entropy of change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27° C is
(*a*) 38.3 J mol^{-1} K^{-1} (*b*) 35.8 J mol^{-1} K^{-1}
(*c*) 32.3 J mol^{-1} K^{-1} (*d*) 42.3 J mol^{-1} K^{-1}
(AIEEE 2011)

B41. The value of enthalpy change (ΔH) for the reaction :
$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$
at 27° C is –1366.5 kJ mol^{-1}. The value of internal energy change for the above reaction at this temperature will be
(*a*) –1369.0 kJ (*b*) –1364.0 kJ
(*c*) –1361.5 kJ (*d*) –1371.5 kJ
(AIEEE 2011)

B42. The standard enthalpies of combustion of $C_6H_6(\ell)$, C(graphite) and $H_2(g)$ are respectively –3270 kJ mol^{-1}, – 394 kJ mol^{-1} and –286 kJ mol^{-1}. What is the standard enthalpy of formation of $C_6H_6(\ell)$ in kJ mol^{-1}?
(*a*) – 48 (*b*) + 48 (*c*) – 480 (*d*) + 480
(*e*) – 72 *(Kerala P.E.T. 2012)*

B43. The incorrect expression among the following is
(*a*) in isothermal proceess, $W_{reversible} = -nRT \ln \frac{V_f}{V_i}$
(*b*) $\ln K = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$
(*c*) $K = e^{-\Delta G^\circ \backslash RT}$
(*d*) $\frac{\Delta G_{system}}{\Delta S_{total}} = -T$ *(A.I.E.E.E. 2012)*

B44. For isothermal expansion of an ideal gas, the correct combination of thermodynamic parameters will be
(*a*) $\Delta U = 0, q = 0, w \neq 0$ and $\Delta H \neq 0$
(*b*) $\Delta U \neq 0, q \neq 0, w \neq 0$ and $\Delta H = 0$
(*c*) $\Delta U = 0, q \neq 0, w = 0$ and $\Delta H \neq 0$
(*d*) $\Delta U = 0, q \neq 0, w \neq 0$ and $\Delta H = 0$
(W.B. JEE. 2013)

Answers

B32. (*d*) **B33.** (*c*) **B34.** (*d*) **B35.** (*b*) **B36.** (*d*) **B37.** (*d*) **B38.** (*b*) **B39.** (*c*) **B40.** (*a*) **B41.** (*b*)
B42. (*b*) **B43.** (*b*) **B44.** (*d*)

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B45. Calculate the enthalpy change for the reaction :
$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$
using the data given below :

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l) \qquad \Delta H = -1415 \text{ kJ}$$

$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H = -1566 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -286 \text{ kJ}$$

(a) – 437 kJ (b) + 35 kJ
(c) – 135 kJ (d) none of these
(J.K. C.E.T. 2013)

B46. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0 °C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be
(R = 8.314 J/mol K) (ln 7.5 = 2.01)
(a) $q = +208$ J, $w = +208$ J
(b) $q = +208$ J, $w = -208$ J
(c) $q = -208$ J, $w = -208$ J
(d) $q = -208$ J, $w = +208$ J *(JEE Main 2013)*

B47. The enthalpy of vaporization of a certain liquid at its boiling point of 35 °C is 24.64 kJ mol^{-1}. The value of change in entropy for the process is
(a) 704 J K^{-1} mol^{-1} (b) 80 J K^{-1} mol^{-1}
(c) 24.64 J K^{-1} mol^{-1} (d) 7.04 J K^{-1} mol^{-1}
(WB JEE 2014)

B48. The value of ΔH for cooling 2 mol of an ideal monoatomic gas from 225 °C to 125 °C at constant pressure will be [given $C_p = \frac{5}{2}R$]
(a) 250 R (b) –500 R
(c) 500 R (d) –250 R *(WB JEE 2014)*

B49. Given that
$C + O_2 \longrightarrow CO_2$; $\Delta H^\circ = -x$ kJ
$2CO + O_2 \longrightarrow 2CO_2$; $\Delta H^\circ = -y$ kJ
The heat of formation of carbon monoxide will be
(a) $\frac{y - 2x}{2}$ (b) $y + 2x$
(c) $2x - y$ (d) $\frac{2x - y}{2}$ *(WB JEE 2014)*

B50. The entropy of vaporization of a liquid is 58 J K^{-1} mol^{-1}. If 100 g of its vapour condenses at its boiling point of 123°C, the value of entropy change for the process is (molar mass of the liquid = 58 mol^{-1}).
(a) –100 J K^{-1} (b) 100 J K^{-1}
(c) –123 J K^{-1} (d) 123 J K^{-1}
(e) 1230 J K^{-1} *(Kerala PET 2014)*

B51. The ratio of heat liberated at 298 K from the combustion of one kg of coke and by burning, water gas obtained from 1 kg of coke is (assume coke to be 100% carbon, enthalpies of combustion of C, CO and H_2 as 393.5 kJ, 285 kJ, 285 kJ respectively all at 298 K).
(a) 0.79 : 1 (b) 0.69 : 1
(c) 0.86 : 1 (d) 0.96 : 1
(Karnataka CET 2014)

B52. At 25°C, the combustion of 1 mol of liquid benzene, the heat of reaction at constant pressure is given by
$C_6H_6(l) + \frac{7}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$
$\Delta H = -780.980$ cal
Calculate the heat of reaction at constant volume
(a) 780.086 kcal (b) –782.470 kcal
(c) –390.043 kcal (d) 390.043 kcal
(AMU Engg. 2014)

B53. For complete combustion of ethanol,
$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$,
the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25°C. Assuming ideality the enthalpy of combustion, $\Delta_C H$, for the reaction will be (R = 8.314 J mol^{-1})
(a) –1350.50 kJ mol^{-1} (b) –1366.95 kJ mol^{-1}
(c) –1361.95 kJ mol^{-1} (d) –1460.50 kJ mol^{-1}
(JEE Main 2014)

B54. For the reaction $X_2Y_4(l) \longrightarrow 2XY_2(g)$ at 300 K the values of ΔU and ΔS are 2.2 kcal and 20 cal K^{-1} respectively. The value of ΔG for the reaction is
(a) – 3400 cal (b) 3400 cal
(c) –2800 cal (d) 2000 cal *(WB JEE 2015)*

B55. Given R = 8.314 JK^{-1} mol^{-1}, the work done during combustion of 0.090 kg of ethane (molar mass = 30) at 300 K is
(a) – 18.7 kJ (b) 18.7 kJ
(c) 6.234 kJ (d) –6.234 kJ
(MH-CET 2015)

B56. What is the amount of work done when two moles of an ideal gas is compressed from a volume of 1 m^3 to 10 dm^3 at 300 K against a pressure of 100 kPa?
(a) 99 kJ (b) –99 kJ
(c) 114.9 kJ (d) –114.9 kJ
(MH-CET 2015)

B57. What is the amount of work done when 0.5 mol of methane, $CH_4(g)$ is subjected to combustion at 300 K? (given, R = 8.314 J K^{-1} mol^{-1}) :
(a) – 2494 J (b) – 4988 J
(c) + 4988 J (d) + 2494 J. *(MH-CET 2016)*

Answers

B45. (c) **B46.** (b) **B47.** (b) **B48.** (b) **B49.** (a) **B50.** (a) **B51.** (b) **B52.** (b) **B53.** (b) **B54.** (c)
B55. (b) **B56.** (a) **B57.** (d)

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B58. The standard enthalpy of formation of $H_2O(l)$ and $Fe_2O_3(s)$ are respectively –286 kJ mol^{-1} and –824 kJ mol^{-1}. What is the standard enthalpy change for the following reaction?

$Fe_2O_3(s) + 3H_2(g) \longrightarrow 3H_2O(l) + 2Fe(s)$

(*a*) – 538 kJ mol^{-1} (*b*) + 538 kJ mol^{-1}
(*c*) – 102 kJ mol^{-1} (*d*) + 34 kJ mol^{-1}
(*e*) – 34 kJ mol^{-1} *(Kerala-PET 2016)*

B59. The correct descending order of the heat liberated (in kJ) during the neutralisation of the acids CH_3COOH (W), HF (X), HCOOH(Y) and HCN (Z) under identical conditions (K_a of $CH_3COOH = 1.8 \times 10^{-5}$, HCOOH = 1.8×10^{-4}, HCN = 4.9×10^{-10} and HF = 3.2×10^{-4}) is

(*a*) Y > X > Z > W (*b*) X > Y > W > Z
(*c*) W > X > Y > Z (*d*) Z > W > Y > X
(*e*) Z > Y > X > W *(Kerala-PET 2016)*

B60. If the bond energies of H–H, Br–Br and H–Br are 433, 192 and 364 kJ mol^{-1} respectively, then ΔH° for the reaction:

$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$ is

(*a*) – 261 kJ (*b*) + 103 kJ
(*c*) + 261 kJ (*d*) – 103 kJ
(Karnataka CET 2016)

B61. The correct statement regarding entropy is

(*a*) at absolute zero temperature, entropy of a perfectly crystalline solid is zero
(*b*) at absolute zero temperature, the entropy of a perfectly crystalline substance is +ve
(*c*) at absolute zero temperature, the entropy of all crystalline substances is zero
(*d*) at 0°C, the entropy of a perfect crystalline solid is zero. *(Karnataka CET 2016)*

B62. The heats of combustion of carbon and carbon monoxide are –393.5 and –283.5 kJ mol^{-1} respectively. The heat of formation (in kJ) of carbon monoxide per mole is

(*a*) 110.5 (*b*) 676.5
(*c*) – 676.5 (*d*) – 110.5 *(JEE Main 2016)*

B63. A reaction has both ΔH and ΔS –ve. The rate of reaction

(*a*) cannot be predicted for change in temperature
(*b*) increases with increase in temperature
(*c*) increases with decrease in temperature
(*d*) remains unaffected by change in temperature
(Karnataka CET 2017)

B64. Mixing of N_2 and H_2 form an ideal gas mixture at room temperature in a container. For this process, which of the following statements is true?

(*a*) $\Delta H = 0$, $\Delta S_{surrounding} = 0$, $\Delta S_{system} = 0$ and ΔG = –ve
(*b*) $\Delta H = 0$, $\Delta S_{surrounding} = 0$, $\Delta S_{system} > 0$ and ΔG = –ve
(*c*) $\Delta H > 0$, $\Delta S_{surrounding} = 0$, $\Delta S_{system} > 0$ and ΔG = –ve
(*d*) $\Delta H < 0$, $\Delta S_{surrounding} > 0$, $\Delta S_{system} < 0$ and ΔG = –ve
(*e*) $\Delta H = 0$, $\Delta S_{surrounding} = 0$, $\Delta S_{system} < 0$ and ΔG = –ve
(Kerala PET 2017)

B65. Given

$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\circ = -393.5$ kJ mol^{-1}

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta_r H^\circ = -285.8$ kJ mol^{-1}

$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g)$;
$\Delta_r H^\circ = +890.3$ kJ mol^{-1}

Based on the above thermochemical equations, the value of $\Delta_r H^\circ$ at 298 K for the reaction

$C_{(graphite)} + 2H_2(g) \longrightarrow CH_4(g)$ will be:

(*a*) + 74.8 kJ (*b*) + 144.0 kJ
(*c*) – 74.8 kJ (*d*) – 144.0 kJ
(JEE Main 2017)

B66. ΔU is equal to

(*a*) isochoric work (*b*) isobaric work
(*c*) adiabatic work (*d*) isothermal work
(JEE Main 2017)

B67. What will be the heat change at constant volume for the reaction whose heat change at constant pressure is –560 *k*cal at 27 °C? The reaction is

$C_8H_{16} + 12O_2 \longrightarrow 8CO_2 + 8H_2O$

(Given R = 2 cal mol^{-1} K^{-1})

(*a*) –557600 calories (*b*) 442800 calories
(*c*) –561800 calories (*d*) 368240 calories
(J.K. CET 2018)

B68. What condition will facilitate the spontaneity of a reaction if ΔH and ΔS both are negative?

(*a*) Low teperature (*b*) High temperature
(*c*) Low pressure (*d*) High pressure
(J.K. CET 2018)

B69. What will be the entropy change of the system when expansion of 1 mole of a gas takes place from 3 L to 6 L under isothermal conditions?
Consider, R = 2 cal K^{-1} mol^{-1} and log 2 = 0.301.

(*a*) 2.84 cal K^{-1} (*b*) 1.386 cal K^{-1}
(*c*) 0.37 cal K^{-1} (*d*) 5.26 cal K^{-1}
(J.K. CET 2018)

B70. The heat of neutralisation of a strong base and a strong acid is 13.7 kcal. The heat released when 0.6 mole HCl solution is added to 0.25 mole of NaOH is

(*a*) 3.425 kcal (*b*) 8.22 kcal
(*c*) 11.645 kcal (*d*) 13.7 kcal
(WB JEE 2018)

B71. During a reversible adiabatic process, the pressure of a gas is found to be proportional to the cube of its absolute temperature. The ratio $\frac{C_p}{C_v}$ for the gas is

(*a*) 3/2 (*b*) 7/2
(*c*) 5/3 (*d*) 9/7 *(WB JEE 2018)*

Answers

B58. (*e*) **B59.** (*b*) **B60.** (*d*) **B61.** (*a*) **B62.** (*d*) **B63.** (*c*) **B64.** (*b*) **B65.** (*c*) **B66.** (*c*) **B67.** (*a*)
B68. (*a*) **B69.** (*b*) **B70.** (*a*) **B71.** (*a*)

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B72. One mole of ethanol is produced reacting graphite, H_2, and O_2 together. The standard enthalpy of formation is –277.7 kJ mol^{-1}. Calculate the standard enthalpy of the reaction when 4 moles of graphite is involved.
(*a*) –277.7 (*b*) –555.4
(*c*) –138.85 (*d*) –69.42
(*e*) –1110.8 *(Kerala PET 2018)*

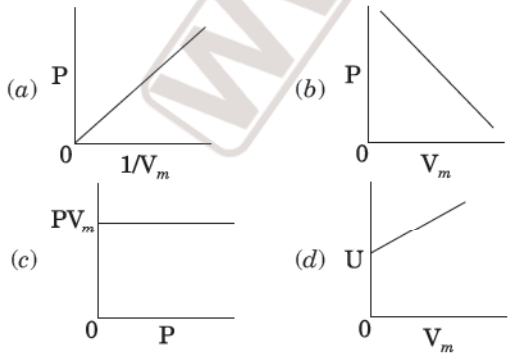
B73. Which of the following process best describes atomization of $CH_4(g)$?
(*a*) Exothermic (*b*) Endothermic
(*c*) Non-spontaneous (*d*) Spontaneous
(*e*) Both (*b*) and (*c*) *(Kerala PET 2018)*

B74. Which of the following can help predict the rate of a reaction if the standard Gibbs' free energy of reaction ($\Delta_r G^\circ$) is known?
(*a*) Equilibrium constant
(*b*) $\Delta_r H^\circ$ (*c*) $\Delta_r U^\circ$
(*d*) Heat liberated during the course of reaction in calorimeter.
(*e*) both (*b*) and (*a*) *(Kerala PET 2018)*

B75. The combustion of benzene (*l*) gives CO_2(g) and $H_2O(l)$. Given that heat of combustion of benzene at constant volume is –3263.9 kJ mol^{-1} at 25° C; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be: (R = 8.314 JK^{-1} mol^{-1})
(*a*) 4152.6 (*b*) –452.46
(*c*) 3260 (*d*) –3267.6 *(JEE Main 2018)*

B76. Given
(*i*) C(graphite) + $O_2(g) \longrightarrow CO_2(g)$ $\Delta_r H^\circ = x$ kJ mol^{-1}
(*ii*) C(graphite) + $\frac{1}{2}O_2(g) \longrightarrow CO(g)$ $\Delta_r H^\circ = y$ kJ mol^{-1}
(*iii*) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ $\Delta_r H^\circ = z$ kJ mol^{-1}
Based on the above thermochemical equations, find out which one of the following algebraic relationship is correct?
(*a*) $z = x + y$ (*b*) $x = y - z$
(*c*) $x = y + z$ (*d*) $y = 2z - x$ *(JEE Main 2019)*

B77. The combination of plots which does not represent isothermal expansion of an ideal gas is :



(JEE Main 2019)

B78. The process with negative entropy change is
(*a*) Dissolution of iodine in water
(*b*) Synthesis of ammonia from N_2 and H_2
(*c*) Dissociation of $CaSO_4(s)$ to $CaO(s)$ and $SO_3(g)$
(*d*) Sublimation of dry ice. *(JEE Main 2019)*

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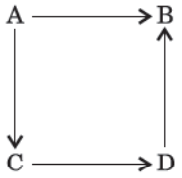
B79. The enthalpy of vaporization of a liquid is 30 kJ mol^{-1} and entropy of vaporization is 75 $Jmol^{-1}$. The boiling point of the liquid at 1 atm is
(*a*) 250 K (*b*) 400 K (*c*) 450 K (*d*) 600 K *(I.I.T. 2004)*

B80. Two moles of an ideal gas is expanded isothermally and reversibly from 1 L to 10 L at 300 K. The enthalpy change (in kJ) for the process is
(*a*) 11.4 kJ (*b*) –11.4 kJ (*c*) 0 kJ (*d*) 4.8 kJ *(I.I.T. 2004)*

B81. The reaction A to B is not feasible but on changing entropy through a series of steps :



ΔS (A → C) = 50 ev, ΔS (C → D) = 30 ev,
ΔS (B → D) = 20 ev.
The entropy change for A → B would be
(*a*) 100 eV (*b*) 60 eV
(*c*) – 60 eV (*d*) – 100 eV *(I.I.T. 2006)*

B82. For the process :
$H_2O(l)$ (1 bar, 373 K) $\longrightarrow$ $H_2O(g)$ (1bar, 373 K), the correct set of thermodynamic parameters is:
(*a*) $\Delta G = 0$, ΔS = +ve (*b*) $\Delta G = 0$, ΔS = –ve
(*c*) ΔG = +ve, $\Delta S = 0$ (*d*) ΔG = –ve, ΔS = +ve *(I.I.T. 2007)*

B83. The species which by definition has zero standard molar enthalpy of formation at 298 K is
(*a*) $Br_2(g)$ (*b*) $Cl_2(g)$
(*c*) $H_2O(g)$ (*d*) $CH_4(g)$ *(I.I.T. 2010)*

B84. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a C ≡ C bond in C_2H_2. That energy is (take the bond energy of a C – H bond as 350 kJ mol^{-1}) :
$2C(s) + H_2(g) \longrightarrow C_2H_2(g)$; ΔH = 225 kJ mol^{-1}
$2C(s) \longrightarrow 2C(g)$; ΔH = 1410 kJ mol^{-1}
$H_2(g) \longrightarrow 2H(g)$; ΔH = 330 kJ mol^{-1}
(*a*) 1165 (*b*) 837
(*c*) 865 (*d*) 815 *(I.I.T. J.E.E. 2012)*

Answers

B72. (*b*) **B73.** (*e*) **B74.** (*a*) **B75.** (*d*) **B76.** (*c*) **B77.** (*c*) **B78.** (*b*) **B79.** (*b*) **B80.** (*b*) **B81.** (*b*)
B82. (*a*) **B83.** (*b*) **B84.** (*d*)

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B85. The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 25°C are –400 kJ/mol, –300 kJ/mol and –1300 kJ/mol respectively. The standard enthalpy of combustion per gram of glucose at 25°C is

(a) + 2900 kJ (b) – 2900 kJ

(c) – 16.11 kJ (d) + 16.11 kJ

(JEE Advance 2013)

B86. For the process $H_2O(l) \longrightarrow H_2O(g)$ at T = 100 °C and 1 atmosphere pressure, the correct choice is

(a) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} > 0$

(b) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} < 0$

(c) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} > 0$

(d) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} < 0$

(JEE Advance 2014)

B87. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in J K^{-1} is (1 L atm = 101.3 J)

(a) 5.763 (b) 1.013

(c) – 1.013 (d) – 5.763

(JEE Advance 2016)

B88. The standard state Gibbs free energies of formation of $C_{(graphite)}$ and $C_{(diamond)}$ at T = 298 K are

$\Delta_f G^\circ[C_{(graphite)}] = 0$ kJ mol^{-1};

$\Delta_f G^\circ[C_{(diamond)}] = 2.9$ kJ mol^{-1}

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite $[C_{(graphite)}]$ to diamond $[C_{(diamond)}]$ reduces its volume by 2×10^{-6} m^3 mol^{-1}. If $C_{(graphite)}$ is converted to $C_{(diamond)}$ isothermally at T = 298 K, the pressure at which $C_{(graphite)}$ is in equilibrium with $C_{(diamond)}$, is [Useful information: 1 J = 1 kg m^2s^{-2}; 1 Pa = 1 kg $m^{-1}s^{-2}$; 1 bar = 10^5 Pa]

(a) 29001 bar (b) 58001 bar

(c) 14501 bar (d) 1450 bar

(JEE Advance 2017)

Answers

B85. (c) **B86.** (b) **B87.** (c) **B88.** (c)

C MULTIPLE CHOICE QUESTIONS *with more than one correct answers*

C1. Which of the following are state functions ?

(a) Enthalpy (b) Heat

(c) Free energy (d) Work

C2. In which of the following processes entropy increases?

(a) $I_2(s) \longrightarrow I_2(g)$

(b) Crystallisation of sugar from sugar solution

(c) $2\ NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

(d) $H_2O(l) \rightleftharpoons H_2O(s)$

C3. Which of the following relations are correct ?

(a) $\Delta S = \dfrac{\Delta H - \Delta T}{T}$ (b) $\Delta S = \dfrac{q_{irrev}}{T}$

(c) $K = e^{\Delta G^\circ/RT}$ (d) $\left(\dfrac{d(\Delta H)}{dT}\right)_p = \Delta C_p$

C4. Which of the following expressions represent the criterion of spontaneity ?

(a) $(dS)_{U,V} < 0$ (b) $(dG)_{T,p} < 0$

(c) $(dU)_{S,V} < 0$ (d) $(dH)_{T,p} < 0$

C5. Which of the following are favourable conditions for spontaneous processes ?

(a) $\Delta H(-), \Delta S(+)$ any magnitude

(b) $\Delta H(-), \Delta S(-)$ $\Delta H < T\Delta S$

(c) $\Delta H(+), \Delta S(+)$ $\Delta H < T\Delta S$

(d) $\Delta H(+), \Delta S(+)$ $\Delta H > T\Delta S$

C6. Among the following, state function(s) is/are

(a) internal energy

(b) irreversible expansion work

(c) reversible expansion work

(d) molar enthalpy

(I.I.T. JEE 2009)

C7. A sample containing 1.0 mol of an ideal gas is expanded isothermally and reversibly to ten times of its original volume in two separate experiments. The expansion is carried out at 300 K and at 600 K respectively. Choose the correct option.

(a) Work done at 600 K is 20 times the work done at 300 K.

(b) Work done at 300 K is twice the work done at 600 K.

(c) Work done at 600 K is twice the work done at 300 K.

(d) $\Delta U = 0$ in both cases.

Answers

C1. (a, c) **C2.** (a, c) **C3.** (a, d) **C4.** (b, c) **C5.** (a, d)
C6. (a, d) **C7.** (c, d)

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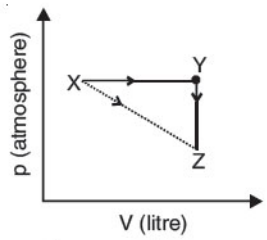
C8. For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct? [Take ΔS as change in entropy and W as work done]



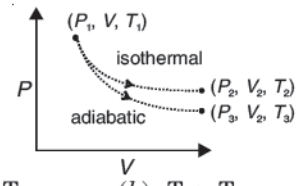
(*a*) $\Delta S_{X\to Z} = \Delta S_{X\to Y} + \Delta S_{Y\to Z}$

(*b*) $W_{X\to Z} = W_{X\to Y} + W_{Y\to Z}$

(*c*) $W_{X\to Y\to Z} = W_{X\to Y}$

(*d*) $\Delta S_{X\to Y\to Z} = \Delta S_{X\to Y}$ *(I.I.T. J.E.E. 2012)*

C9. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is(are) correct?



(*a*) $T_1 = T_2$ (*b*) $T_3 > T_1$

(*c*) $W_{isothermal} > W_{adiabatic}$

(*d*) $\Delta U_{isothermal} > \Delta U_{adiabatic}$ *(I.I.T. J.E.E. 2012)*

C10. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are)

(*a*) ΔG is positive (*b*) ΔS_{system} is positive

(*c*) $\Delta S_{surroundings} = 0$ (*d*) $\Delta H = 0$

(JEE Advance 2013)

C11. For a spontaneous process, the correct statement(s) is (are)

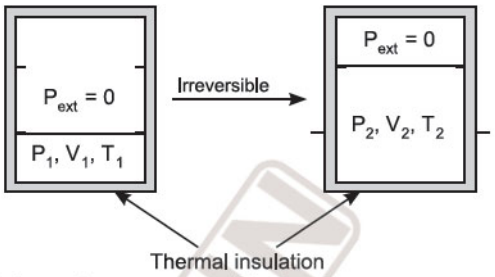
(*a*) $(\Delta G_{system})_{T,P} > 0$

(*b*) $(\Delta G_{system}) + (\Delta S_{surroundings}) > 0$

(*c*) $(\Delta G_{system})_{T,P} < 0$

(*d*) $(\Delta U_{system})_{T,P} > 0$ *(WB JEE 2014)*

C12. An ideal gas in a thermally insulated vessel at internal pressure = P_1, volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of gas are P_2, V_2 and T_2, respectively. For this expansion,



(*a*) $q = 0$ (*b*) $T_2 = T_1$

(*c*) $P_2V_2 = P_1V_1$ (*d*) $P_2P_2^{\gamma} = P_1V_1^{\gamma}$

(JEE Advance 2014)

C13. An ideal gas is expanded from (p_1, V_1, T_1) to (p_2, V_2, T_2) under different conditions. The correct statement(s) among the following is(are)

(*a*) if the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic.

(*b*) the work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions.

(*c*) the work done on the gas is maximum when it is compressed irreversibly from (p_2, V_2) to (p_1, V_1) against constant pressure p_1.

(*d*) the change in internal energy of the gas is (*i*) zero, if it is expanded reversibly with $T_1 = T_2$, and (*ii*) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$.

(JEE Advance 2017)

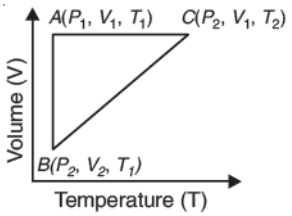
C14. Among the following, the extensive variables are

(*a*) H (enthalpy) (*b*) P (pressure)

(*c*) U (internal energy) (*d*) V (volume)

(WB JEE 2018)

C15. A reversible cyclic process for an ideal gas is shown below. Here, P, V and T are pressure, volume and temperature, respectively. The thermodynamic parameters q, w, H and U are heat, work, enthaply and internal energy, respectively.



The correct option(s) is (are)

(*a*) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = P_2(V_2 - V_1)$

(*b*) $w_{BC} = P_2(V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$

(*c*) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$

(*d*) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

(JEE Advance 2018)

Answers

C8. (*a*, *c*) **C9.** (*a*, *c*, *d*) **C10.** (*b*, *c*, *d*) **C11.** (*b*, *c*) **C12.** (*a*, *b*, *c*) **C13.** (*a*, *b*, *c*) **C14.** (*a*, *c*, *d*) **C15.** (*b*, *c*)

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D MULTIPLE CHOICE QUESTIONS
based on the given passage/comprehension

Passage I.

The first law of thermodynamics merely indicates that in any process there is an exact equivalence between the various forms of energies involved but does not provide any information about the spontaneity of the process. The spontaneity of a process is predicted on the basis of Gibb's free energy change which is related to enthalpy change and entropy change as

$$\Delta G = \Delta H - T\Delta S$$

For a process to be spontaneous, at constant temperature and pressure, there must be decrease in the free energy of the system in the direction of the process i.e., $\Delta G_{p,T} < 0$. $\Delta G_{p,T} > 0$ implies the non-spontaneity condition while $\Delta G_{p,T} = 0$ corresponds to equilibrium condition. The magnitude of ΔH does not change much with change in temperature but the entropy factor $T\Delta S$ changes appreciably indicating that spontaneity depends very much on temperature. The standard free energy change is related to equilibrium constant K as

$$K = e^{-\Delta G^\circ/RT}$$

Answer the following questions :

D1. For the reaction : $CaCO_3(s) \longrightarrow CO_2(g) + CaO(s)$, the signs of ΔH and ΔS respectively are :

(*a*) +, – (*b*) +, +

(*c*) –, – (*d*) –, +

D2. The ΔG values for the following reactions at 800°C are

$S_2(g) + 2O_2(g) \longrightarrow 2SO_2(g)$ $\Delta G = -544$ kJ

$2Zn(s) + S_2(s) \longrightarrow 2ZnS(s)$ $\Delta G = -293$ kJ

$2Zn(s) + O_2(g) \longrightarrow 2ZnO(s)$ $\Delta G = -480$ kJ

The ΔG for the reaction :

$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$ is

(*a*) – 731 kJ (*b*) –773 kJ

(*c*) – 229 kJ (*d*) – 357 kJ

D3. For the equilibrium $H_2O(l) \rightleftharpoons H_2O(g)$ at 1 atm and 298 K

(*a*) Standard free energy change is equal to zero ($\Delta G^\circ = 0$)

(*b*) Free energy change is less than zero ($\Delta G < 0$)

(*c*) Standard free energy change is less than zero ($\Delta G^\circ < 0$)

(*d*) Standard free energy change is greater than zero ($\Delta G^\circ > 0$)

D4. For the water gas reaction :

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$

ΔG° at 1000 K = – 8.1 kJ. The equilibrium constant K is

(*a*) 0.423 (*b*) 4.23

(*c*) 2.64 (*d*) 4.63

D5. If ΔG° is zero for a reaction, then

(*a*) $\Delta H^\circ = 0$ (*b*) $\Delta S^\circ = 0$

(*c*) K (equilibrium constant) = 0

(*d*) K (equilibrium constant) = 1

D6. Which of the following conditions is not favourable for a spontaneous reaction ?

(*a*) ΔH = +ve, $T\Delta S$ = +ve and $T\Delta S > \Delta H$

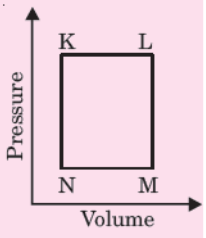
(*b*) ΔH = +ve, $T\Delta S$ = +ve and $T\Delta S < \Delta H$

(*c*) ΔH = –ve, $T\Delta S$ = +ve and $T\Delta S > \Delta H$

(*d*) ΔH = –ve, $T\Delta S$ = –ve and $T\Delta S < \Delta H$

Passage II.

A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.



Answer the following questions:

D7. The pair of isochoric processes among the transformation of states is

(*a*) K to L and L to M

(*b*) L to M and N to K

(*c*) L to M and M to N

(*d*) M to N and N to K

D8. The succeeding operations that enable this transformation of states are

(*a*) heating, cooling, heating, cooling

(*b*) cooling, heating, cooling, heating

(*c*) heating, cooling, cooling, heating

(*d*) cooling, heating, heating, cooling.

Answers

Passage-I **D1.** (*a*) **D2.** (*a*) **D3.** (*d*) **D4.** (*c*) **D5.** (*d*) **D6.** (*b*) **Passage-II** **D7.** (*b*) **D8.** (*c*)

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Assertion Reason Type Questions

The questions given below consist of an Assertion and the Reason. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
(*b*) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.
(*c*) If assertion is CORRECT, but reason is INCORRECT.
(*d*) If assertion is INCORRECT, but reason is CORRECT.
(*e*) If both assertion and reason are INCORRECT.

I.

1. Assertion : Enthalpy of neutralisation for both HNO_3 and HCl with NaOH is 57.1 kJ/mole.
Reason : NaOH is strong electrolyte.

2. Assertion : Standard enthalpy of graphite is lower than that of diamond.
Reason : Standard enthlapy of elements is taken to be zero arbitrarily.

3. Assertion : Work is a sate function.
Reason : Work does not depend upon the path.

4. Assertion : Endothermic compounds are more stable than exothermic compouonds.
Reason : Endothermic reactions have positive enthalpy of formation.

5. Assertion : Enthalpy of combustion is always negative
Reason : Combustion reactions proceeds with evolution of heat.

6. Assertion : Both internal energy and enthalpy and state functions.
Reason : Internal energy and entahlpy are extensive properties.

7. Assertion : In a cyclic process $\Delta U = 0$.
Reason : Cyclic process represents equilibrium state.

8. Assertion : Internal energy change in the heat evolved or absorbed at consatant pressure.
Reason : Internal energy is state function.

9. Assertion : For the combustion of methane, $\Delta E > \Delta H$.
Reason : ΔH is related to ΔE by the expression, $\Delta H = \Delta E + \Delta n_g RT$ *(A.I.I.M.S. 2007)*

II.

1. Assertion : Decrease in free energy causes spontaneous reaction.
Reason : Spontaneous reactions are invariably exothermic reactions.

2. Assertion : Both ΔH and ΔU are state functions.
Reason : A state function depends only on the initial and final states of the system and is independent of the path.

3. Assertion : The temperature of a gas does not change when it undergoes an adiabatic expansion.
Reason : During an adiabatic process, heat energy is not exchanged between a system and its surroundings.

4. Assertion : The increase in internal energy (ΔU) for the vaporisation of one mole of water at 1 atm at 373K is zero.
Reason : For all isothermal processes, $\Delta U = 0$ *(A.I.I.M.S. 2003)*

5. Assertion : Many endothermic reactions which are non- spontaneous at room temperature become spontaneous on increasing the temperature.
Reason : Endothermic reactions become spontaneous at high temperature if ΔS is +ve and $T\Delta S > \Delta H$.

6. Assertion : Decrease in free energy during the process under particular conditions provides a measure of its spontaneity.
Reason : For a spontaneous reaction, ΔS_{total} must be +ve.

7. Assertion : In a reversible process, $\Delta S_{universe}$ is zero.
Reason : Entropy is an extensive property.

8. Assertion : At equilibrium, ΔG becomes zero.
Reason : At equilibrium, the two tendencies ΔH and $T\Delta S$ become equal and opposite.

9. Assertion : For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.
Reason : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. *(I.I.T. JEE 2008)*

10. Assertion : There is a natural asymmetry between converting work to heat and converting heat to work.
Reason : No process is possible in which the sole result is the absorption of heat from a reservoir and is complete conversion into work. *(I.I.T. JEE 2008)*

11. Assertion : Spontaneous process is an irreversible process and may be reversed by some external agency.
Reason : Decrease in enthalpy is a contributory factor for spontaneity.

12. Assertion : A liquid crystallises into a solid and is accompanied by decrease in entropy.
Reason : In crystals, molecules organise in an ordered manner.

Answers

I.	**1.** (*b*)	**2.** (*b*)	**3.** (*d*)	**4.** (*d*)	**5.** (*a*)	**6.** (*b*)	**7.** (*c*)	**8.** (*d*)	**9.** (*a*)			
II.	**1.** (*c*)	**2.** (*a*)	**3.** (*d*)	**4.** (*d*)	**5.** (*a*)	**6.** (*b*)	**7.** (*b*)	**8.** (*a*)	**9.** (*d*)	**10.** (*d*)	**11.** (*b*)	**12.** (*a*)

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Matching Type Questions

1. Match the enteries of processes given in List-I with the description given in List-II and choose the correct option (*a*), (*b*), (*c*) and (*d*) given in code.

List-I	List-II
(P) Isobaric process	(1) process in which driving force is very different than opposing force.
(Q) Isothermal process	(2) process in which no heat enters or leaves the system.
(R) Adibatic process constant.	(3) process in which temperature of the system remains
(S) Irreversible process	(4) A process in which pressure of the system is kept constant

Code

	P	Q	R	S
(*a*)	4	3	1	2
(*b*)	4	3	2	1
(*c*)	3	4	2	1
(*d*)	3	4	1	2

2. Match the sign of ΔH and ΔS given in **List-I** with the type of reaction given in **List II** and select the correct option.

List-I	List-II
(P) +ve and +ve	**1.** Spontaneous at all temperatures.
(Q) –ve and –ve	**2.** Non spontaneous at all temperatures.
(R) +ve and –ve	**3.** Spontaneous only at low temperature.
(S) –ve and +ve	**4.** Spontaneous only at high temperature.

Code

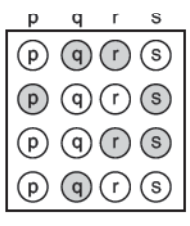
	P	Q	R	S
(*a*)	4	2	3	1
(*b*)	3	4	2	1
(*c*)	3	4	1	2
(*d*)	4	3	2	1

Answers

1. (*b*) **2.** (*d*)

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.



If the correct matches are A-*q*, A-*r*, B-*p*, B-*s*, C-*r*, C-*s* and D-*q*, then the correctly bubbled matrix will look like the following:

1. Match the term given in Column I with the equation given in Column II

Column I	Column II
(A) Enthalpy of formation	(*p*) $CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4.5H_2O$
(B) Enthalpy of combustion	(*q*) $CuSO_4(s) + nH_2O(l) \longrightarrow CuSO_4\ (aq)$
(C) Enthalpy of solution	(*r*) $C(s) + O_2(g) \longrightarrow CO_2(g)$
(D) Enthalpy of hydration	(*s*) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

2. Match the following :

Column I	Column II
(*a*) Entropy of vapourisation	(*p*) decreases
(*b*) K for spontaneous process	(*q*) is always positive
(*c*) Crystalline solid state	(*r*) lowest entropy
(*d*) ΔU in adiabatic expansion of ideal gas	(*s*) $\frac{\Delta H_{vap}}{T_b}$

3. Match the term given in column I with its description in Column II.

Column I	Column II
(*a*) Path function	(*p*) Heat
(*b*) State function	(*q*) Internal energy
(*c*) Intensive property	(*r*) Entropy
(*d*) Extensive property	(*s*) Specific heat

4. Match the process given in Column-I with the entropy change in Column-II :

Column I	Column II
(*a*) Reversible adiabatic ideal gas compression.	(*p*) $\Delta S_{surr} = 0$
(*b*) Reversible isothermal ideal gas expansion.	(*q*) $\Delta S_{system} = 0$
(*c*) Adiabatic free expansion ($p_{ext} = 0$) of an ideal gas.	(*r*) $\Delta S_{surr} > 0$
(*d*) Irreversible isothermal ideal gas compression.	(*s*) $\Delta S_{surr} < 0$

Answers

(1) : (A) – (*r*) (B) – (*r*), (*s*) (C) – (*q*) (D) – (*p*)
(2) : (A) – (*q*) (*s*) (B) – (*q*) (C) – (*r*) (D) – (*p*)
(3) : (A)–(*p*) (B)–(*q*), (*r*) (C)–(*p*), (*s*) (D)–(*q*), (*r*)
(4) : (A) – (*p*), (*q*) (B) – (*s*); (C) – (*p*) (D) – (*r*)

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Integer Type Questions

Integer Type: The answer to each of the following question is a **single-digit**-integer ranging from 0 to 9.

1. The number of properties which are state functions among the following is :

   Enthalpy, entropy, pressure, volume, heat, internal energy, temperature, molar heat capacity, work, free energy.

2. The number of intensive properties among the following is

   Density, temperature, volume, pressure, enthalpy, entropy, viscosity, force, molar heat capacity, free energy, heat capacity.

3. The difference between C_p and C_v for a diatomic gas is nR. The value of n is

4. A tank contains 10^5L of water. The amount of energy required to raise the temperature of water from 15°C to 25°C is $n \times 10^6$ kJ (assume specific heat capacity of water 4 $J°C^{-1}g^{-1}$. The value of n is

5. The change in internal energy when 2.0 mole of an ideal gas at 25°C are compressed isothermally and reversibly from 1 bar to 2 bar is

6. All the energy released from the reaction X → Y, $\Delta_r G° = -193$ kJ mol^{-1} is used for oxidizing M^+ as $M^+ \rightarrow M^{3+} + 2e^-$, $E° = -0.25$ V. Under standard conditions, the number of moles of M^+ oxidized when one mole of X is converted to Y is

   [F = 96500 C mol^{-1}] *(JEE Advance 2015)*

Answers

1. 7 **2.** 5 **3.** 1 **4.** 4 **5.** 0 **6.** 4

NCERT Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

1. Thermodynamics is not concerned about _____.
   (*a*) energy changes involved in a chemical reaction.
   (*b*) the extent to which a chemical reaction proceeds.
   (*c*) the rate at which a reaction proceeds.
   (*d*) the feasibility of a chemical reaction.
2. Which of the following statements is correct ?
   (*a*) The presence of reacting species in a covered beaker is an example of open system.
   (*b*) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
   (*c*) The presence of reactants in a closed vessel made up of copper is an example of a closed system.
   (*d*) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.
3. The state of a gas can be described by quoting the relationship between _____ .
   (*a*) pressure, volume, temperature
   (*b*) temperature, amount, pressure
   (*c*) amount, volume, temperature
   (*d*) pressure, volume, temperature, amount
4. The volume of gas is reduced to half from its original volume. The specific heat will be _____ .
   (*a*) reduced to half (*b*) be doubled
   (*c*) remain constant (*d*) increased four times

Answers

1. (*c*) **2.** (*c*) **3.** (*d*) **4.** (*c*)

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5. During complete combustion of one mole of butane, 2658 kJ of heat is released. The thermochemical reaction for above change is

(*a*) $2C_4H_{10}(g)\ 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(l)$
$\Delta_cH = -2658.0\ kJ\ mol^{-1}$

(*b*) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(g)$
$\Delta_cH = -1329.0\ kJ\ mol^{-1}$

(*c*) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$
$\Delta_cH = -2658.0\ kJ\ mol^{-1}$

(*d*) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$
$\Delta_cH = +2658.0\ kJ\ mol^{-1}$

6. $\Delta_fU°$ of formation of $CH_4(g)$ at certain temperature is $-393\ kJ\ mol^{-1}$. The value of $\Delta_fH°$ is

(*a*) zero (*b*) $< \Delta_fU°$
(*c*) $> \Delta_fU°$ (*d*) equal to $\Delta_fU°$

7. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.

(*a*) $q = 0, \Delta T \neq 0, w = 0$ (*b*) $q \neq 0, \Delta T = 0, w = 0$
(*c*) $q = 0, \Delta T = 0, w = 0$ (*d*) $q = 0, \Delta T < 0, w \neq 0$

8. The pressure-volume work for an ideal gas can be calculated by using the expression $w = -\int_{V_i}^{V_f} p_{ex}dV$. The work can be calculated from the pV – plot by using the area under the curve within the specified limits. When an ideal gas is compressed (*a*) reversibly or (*b*) irreversibly from volume V_i to V_f; choose the correct option.

(*a*) w (reversible) = w (irreversible)
(*b*) w (reversible) < w (irreversible)
(*c*) w (reversible) > w (irreversible)
(*d*) w (reversible) = w (irreversible) + $p_{ex}.\Delta V$

9. The entropy change can be calculated by using the expression $\Delta S = \frac{q_{rev}}{T}$. When water freezes in a glass beaker, choose the correct statement amongst the following :

(*a*) ΔS (system) decreases but ΔS (surroundings) remains the same.
(*b*) ΔS (system) increases but ΔS (surroundings) decreases.
(*c*) ΔS (system) decreases but ΔS (surroundings) increases.
(*d*) ΔS (system) decreases but ΔS (surroundings) also decreases.

10. On the basis of thermochemical equations (a), (b) and (c), find out which of the algebric relationships given in options (*i*) to (*iv*) is correct.

(*i*) C (graphite) + $O_2(g) \longrightarrow CO_2(g)$; $\Delta_rH = x\ kJ\ mol^{-1}$

(*ii*) C (graphite) + $\frac{1}{2}O_2(g) \longrightarrow CO(g)$; $\Delta_rH = y\ kJ\ mol^{-1}$

(*iii*) C (*g*) + $\frac{1}{2}O_2(g) \longrightarrow CO_2(g)$; $\Delta_rH = z\ kJ\ mol^{-1}$

(*a*) $z = x + y$ (*b*) $x = y - z$
(*c*) $x = y + z$ (*d*) $y = 2z - x$

11. Consider the reactions given below. On the basis of these reactions find out which of the algebric relations given in options (*i*) to (*iv*) is correct ?

(*i*) C (g) + 4H(*g*) $\longrightarrow CH_4(g)$; $\Delta_rH = x\ kJ\ mol^{-1}$
(*ii*) C (graphite) + $2H_2(g) \longrightarrow CH_4(g)$; $\Delta_rH = y\ kJ\ mol^{-1}$

(*a*) $x = y$ (*b*) $x = 2y$
(*c*) $x > y$ (*d*) $x < y$

12. The enthalpies of elements in their standard states are taken as zero. The enthalpy of formation of a compound

(*a*) is always negative
(*b*) is always positive
(*c*) may be positive or negative
(*d*) is never negative

13. Enthalpy of sublimation of a substance is equal to

(*a*) enthalpy of fusion + enthalpy of vaporisation
(*b*) enthalpy of fusion
(*c*) enthalpy of vaporisation
(*d*) twice the enthalpy of vaporisation

14. Which of the following is not correct ?

(*a*) ΔG is zero for a reversible reaction
(*b*) ΔG is positive for a spontaneous reaction
(*c*) ΔG is negative for a spontaneous reaction
(*d*) ΔG is positive for a non-spontaneous reaction

Answers

5. (*c*) **6.** (*b*) **7.** (*c*) **8.** (*b*) **9.** (*c*) **10.** (*c*) **11.** (*c*) **12.** (*c*) **13.** (*a*) **14.** (*b*)

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Multiple Choice Questions (Type-II)

15. Thermodynamics mainly deals with
(*a*) interrrelation of various forms of energy and their transformation from one form to another.
(*b*) energy changes in the processes which depend only on initial and final states of the microscopic systems containing a few molecules.
(*c*) how and at what rate these energy transformations are carried out.
(*d*) the system in equilibrium state or moving from one equilibrium state to another equilibrium state.

16. In an exothermic reaction, heat is evolved, and system loses heat to the surrounding. For such system
(*a*) q_p will be negative (*b*) $\Delta_r H$ will be negative
(*c*) q_p will be positive (*d*) $\Delta_r H$ will be positive

17. The spontaneity means, having the potential to proceed without the assistance of external agency. The processes which occur spontaneously are
(*a*) flow of heat from colder to warmer body
(*b*) gas in a container contracting into one corner
(*c*) gas expanding to fill the available volume
(*d*) burning carbon in oxygen to give carbon dioxide.

18. For an ideal gas, the work of reversible expansion under isothermal condition can be calculated by using the expression $w = -nRT \ln \frac{V_f}{V_i}$
A sample containing 1.0 mol of an ideal gas is expanded isothermally and reversibly to ten times of its original volume, in two separate experiments. The expansion is carried out at 300 K and at 600 K respectively. Choose the correct option
(*a*) Work done at 600 K is 20 times the work done at 300 K.
(*b*) Work done at 300 K is twice the work done at 600 K.
(*c*) Work done at 600 K is twice the work done at 300 K.
(*d*) $\Delta U = 0$ in both cases.

19. Consider the following reaction between zinc and oxygen and choose the correct options out of the options given below :
$2Zn(s) + O_2(g) \longrightarrow 2ZnO(s) \quad \Delta H = -693.8 \text{ kJ mol}^{-1}$
(*a*) The enthalpy of two moles of ZnO is less than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.
(*b*) The enthalpy of two moles of ZnO is more than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.
(*c*) 693.8 kJ mol^{-1} energy is evolved in the reaction.
(*d*) 693.8 kJ mol^{-1} energy is absorbed in the reaction.

Answers

15. (*a, d*) **16.** (*a, b*) **17.** (*c, d*) **18.** (*c, d*) **19.** (*a, c*)

Matching Type Questions

In the following question more than one correlation is possible between options of both columns.

20. Match the following :

A	B
(*i*) Adiabatic process	(*a*) Heat
(*ii*) Isolated system	(*b*) At constant volume
(*iii*) Isothermal change	(*c*) First law of thermodynamics
(*iv*) Path function	(*d*) No exchange of energy and matter
(*v*) State function	(*e*) No transfer of heat
(*vi*) $\Delta U = q$	(*f*) Constant temperature
(*vii*) Law of conservation of energy	(*g*) Internal energy
(*viii*) Reversible process	(*h*) $p_{ext} = 0$
(*ix*) Free expansion	(*i*) At constant pressure
(*x*) $\Delta H = q$	(*j*) Infinitely slow process which proceeds through a series of equilibrium states
(*xi*) Intensive property	(*k*) Entropy
(*xii*) Extensive property	(*l*) Pressure
	(*m*) Specific heat

21. Match the following processes with entropy change :

Reaction	Entropy change
(*i*) A liquid vapourises	(*a*) $\Delta S = 0$
(*ii*) Reaction is non-spontaneous at all temperatures and ΔH is positive	(*b*) ΔS = positive
(*iii*) Reversible expansion of an ideal gas	(*c*) ΔS = negative

22. Match the following parameters with description for spontaneity :

Δ (Parameters) $\Delta_r H°$	$\Delta_r S°$	$\Delta_r G°$	Description
(*i*) +	–	+	(*a*) Non-spontaneous at high temperature
(*ii*) –	–	+ at high T	(*b*) Spontaneous at all temperatures
(*iii*) –	+	–	(*c*) Non-spontaneous at all temperatures

23. Match the following :

(*i*) Entropy of vapourisation	(*a*) decreases
(*ii*) K for spontaneous process	(*b*) is always positive
(*iii*) Crystalline solid state	(*c*) lowest entropy
(*iv*) ΔU in adiabatic expansion of ideal gas	(*d*) $\frac{\Delta H_{vap}}{T_b}$

Answers

20. (*i*)–(*e*); (*ii*)–(*d*); (*iii*)–(*f*); (*iv*)–(*a*); (*v*)–(*g*), (*k*), (*l*); (*vi*)–(*b*); (*vii*)–(*c*); (*viii*)–(*f*); (*ix*)–(*h*); (*x*)–(*i*); (*xi*)–(*a*), (*l*), (*m*); (*xii*)–(*g*), (*k*)
21. (*i*)–(*b*); (*ii*)–(*c*); (*iii*)–(*a*) **22.** (*i*)–(*c*); (*ii*)–(*a*); (*iii*)–(*b*) **23.** (*i*)–(*b*), (*d*); (*ii*)–(*b*); (*iii*)–(*c*); (*iv*)–(*a*)

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Assertion and Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

(*a*) Both A and R are true and R is the correct explanation of A.
(*b*) Both A and R are true but R is not the correct explanation of A.
(*c*) A is true but R is false.
(*d*) A is false but R is true.

24. Assertion (A) : Combustion of all organic compounds is an exothermic reaction.
Reason (R) : The enthalpies of all elements in their standard state are zero.

25. Assertion (A) : Spontaneous process is an irreversible process and may be reversed by some external agency.
Reason (R) : Decrease in enthalpy is a contributory factor for spontaneity.

26. Assertion (A) : A liquid crystallises into a solid and is accompanied by decrease in entropy.
Reason (R) : In crystals, molecules organise in an ordered manner.

Answers

24. (*b*) **25.** (*b*) **26.** (*a*)

Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A1. (*c*) $\Delta H = \Delta U + \Delta n_g RT$
$\Delta n_g = 2 - (1 + 3) = -2$
$\therefore \quad \Delta H = \Delta U - 2\,RT$
$\therefore \quad \Delta H < \Delta U$

A4. (*c*) For free expansion,
$w = 0$
For adiabatic, $q = 0$
$\Delta U = q + w = 0$
Since internal energy remains contant,

A7. (*a*) $\Delta_r H^\circ = 2\Delta_r H^\circ (H_2O) + \Delta_r H^\circ (O_2) - 2\Delta_r H^\circ (H_2O_2)$
$= 2 \times (-286) + 0 - 2(-188) = \mathbf{-196\ kJ}$

A8. (*a*) Since container is closed and insulated, the process is adiabatic so that $q = 0$
$\Delta U = q + w$
$\Delta U = w \neq 0$

A9. (*a*) : A ⟶ B (constant V) isochoric
B ⟶ C (constant p) isobaric
C ⟶ A (constant T) isothermal.

A10. (*a*) : Work done,
$w = -p\Delta V$
$= -10^5\ Nm^{-2}\,(10^{-2}m^3 - 10^{-3}m^3)$
$= -9 \times 10^2 = -900\ Nm = \mathbf{-900\ J}$

A11. (*c*) Molecular mass of $C_6H_6 = 12 \times 6 + 1 \times 6 = 78$
Heat energy change for burning 78 *g* of C_6H_6
$= -3264.6$ kJ
Heat energy change for burning 39 *g* of C_6H_6
$= \dfrac{-3264.6 \times 39}{78} = \mathbf{-1632.3\ kJ}$

A14. (*a*) (*i*) $C(s) + O_2(g) \longrightarrow CO_2(g)$
$\Delta H = -394\ kJ\ mol^{-1}$
(*ii*) $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$
$\Delta H = -284.5\ kJ\ mol^{-1}$
Subtracting eqn. (*ii*) from eqn. (*i*)
$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$
$\Delta H = \mathbf{-109.5\ kJ\ mol^{-1}}$

A16. (*a*) Specific heat capacity $= \dfrac{\text{Molar heat capacity}}{\text{Molar mass}}$
$= \dfrac{110.4\ JK}{46}$
$= 2.4\ JK^{-1}\ mol^{-1}$

A17. (*c*) Enthalpy of formation for 2 mol of NH_3
$= 2 \times -46.0 = -92.0$ kJ
Enthalpy change for the reaction = 92.0 kJ
(∵ It is reverse reaction)

A18. (*b*) $\Delta H^\circ = \Delta_f H^\circ (CO) + \Delta_f H^\circ (H_2O) - \Delta_f H^\circ(CO_2) - \Delta_f H^\circ (H_2)$
$= -110.5 + (-241.8) - (-393.5) - 0$
$= 41.2$ kJ

A19. (*b*) Heat evolved for neutralisation of H_2SO_4 ($2H^+$) will be doubled the heat evolved for neutralisation of HCl (H^+) *i.e.*,
$y = 2x$ or $x = 0.5\,y$

A22. (*a*) The required equation is :
$H_2O(l) \longrightarrow H_2O(g)$
(*i*) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$
$\Delta H = -285.77$ kJ
(*ii*) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$
$\Delta H = -241.84\ kJ$
Subtracting eqn. (*i*) from eqn. (*ii*)
The enthalpy of vaporisation $= -241.84 - (-285.77)$
$= +43.93\ kJ\ mol^{-1}$

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A23. (*c*) (*i*) $C + O_2 \longrightarrow CO_2$ $\Delta H = -x$ kJ
(*ii*) $2CO + O_2 \longrightarrow 2CO_2$ $\Delta H = -y$ kJ
The required equation is

$$C + \frac{1}{2}O_2 \longrightarrow CO \qquad \Delta H = ?$$

Dividing eqn. (*ii*) by 2

(*iii*) $$CO + \frac{1}{2}O_2 \longrightarrow CO_2 \qquad \Delta H = -y/2 \text{ kJ}$$

Subtract eqn. (*iii*) from eqn. (*i*)

$$C + \frac{1}{2}O_2 \longrightarrow CO \qquad \Delta H = -x + y/2$$

$$\text{or } = \frac{y-2x}{2}$$

A24. (*a*) The required equation is

$$CS_2 + 3O_2 \longrightarrow CO_2 + 2SO_2$$

(*i*) $C + 2S \longrightarrow CS_2$ $\Delta H = 117$ kJ
(*ii*) $C + O_2 \longrightarrow CO_2$ $\Delta H = -393$ kJ
(*iii*) $S + O_2 \longrightarrow SO_2$ $\Delta H = -297$ kJ
Multiply eqn. (*iii*) by 2 and subtract eqn. (*i*) from it
(*iv*) $CS_2 + 2O_2 \longrightarrow C + 2SO_2$ $\Delta H = -711$ kJ
Add eqn. (*ii*) to eqn. (*iv*)

$$CS_2 + 3O_2 \longrightarrow CO_2 + 2SO_2 \qquad \Delta H = \mathbf{-1104\ kJ}$$

A25. (*d*) Heat liberated by burning 5 *g* of S = 46 kJ
Heat liberated by burning 32 *g* of S

$$= \frac{46\times32}{5} \text{ kJ} = 294.4 \text{ kJ}$$

∴ Enthalpy of formation of SO_2

$$= \mathbf{-294.4\ kJ\ mol^{-1}}$$

A27.(*e*) : Molar mass of butane, $C_4H_{10} = 12 \times 4 + 1 \times 10$

$$= \mathbf{58\ g\ mol^{-1}}$$

58 g of butane gives 2658 kJ of heat energy.
14 kg of butane will give heat energy

$$= \frac{2658}{58} \times 14 \times 10^3$$

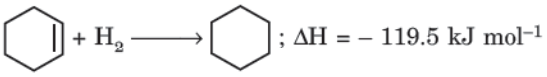
$$= 641.5862 \times 10^3 \text{ kJ}$$

Daily energy requirement for cooking = 20,000 kJ

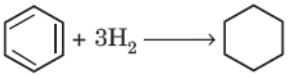
$$= 2 \times 10^4 \text{ kJ}$$

$$\text{No. of days cylinder will last} = \frac{641.5862\times10^3 \text{kJ}}{2\times10^4 \text{kJ day}^{-1}}$$

$$= \mathbf{32.08\ days.}$$

A28.(*a*) :  ; $\Delta H = -119.5$ kJ mol^{-1}

Cyclohexene Hydrogenation

 ; $\Delta H = ?$

If benzene is considered as cyclohexatriene, the observed enthalpy of hydrogenation

$$= 3 \times (-119.5) = -358.5 \text{ kJ mol}^{-1}$$

Resonance energy = Calculated $\Delta H°$(reaction) – Observed $\Delta H°$ (reaction)

∴ Observed $\Delta H°$ (reaction)
= Calculated $\Delta H°$ (reaction) – Resonance energy
= –358.5 – (–150.4) = **–208.1 kJ.**

A29. (*b*) : 0.5 mol $HNO_3 \equiv$ 0.5 mol H^+

$H^+ + OH^- \longrightarrow H_2O$; $\Delta H = -57.1$ kJ

Here OH^- = 0.3 mol. Therefore, OH^- is the limiting reactant.

When 1 mol of OH^- ions are neutralised, heat released = 57.1 kJ

For 0.3 mol of OH^- ions, heat released = 57.1 × 0.3

$$= \mathbf{17.13\ kJ}$$

A30. (*c*) : Let the bond dissociation energy of XY, X_2 and Y_2 be *x*, *x* and 0.5 *x* respectively

$$\frac{1}{2}X_2 + \frac{1}{2}Y_2 \longrightarrow XY \qquad \Delta_f H = -200 \text{ kJ mol}^{-1}$$

$$\Delta H = \frac{1}{2} \text{ B.E } (X_2) + \frac{1}{2} \text{ B.E } (Y_2) - \text{B.E (XY)}$$

$$-200 = \frac{1}{2}x + \frac{0.5x}{2} - x$$

or $-0.25x = -200$

$$x = \frac{200}{0.25} = \mathbf{800\ kJ\ mol^{-1}}$$

A31. (*b*) : (*i*) $Cl_2(g) \longrightarrow 2Cl(g)$, $\Delta H = 242.3$ kJ mol^{-1}
(*ii*) $I_2(s) \longrightarrow I_2(g)$, $\Delta H = 62.76$ kJ mol^{-1}
(*iii*) $I_2(g) \longrightarrow 2I(g)$, $\Delta H = 151.10$ kJ mol^{-1}
(*iv*) $ICl(g) \longrightarrow I(g) + Cl\ (g)$, $\Delta H = 211.3$ kJ mol^{-1}
The required equation is

$$\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \longrightarrow ICl\ (g)$$

Add eq. (*i*) and (*ii*)

(*v*) $Cl_2(g) + I_2(s) \longrightarrow 2Cl(g) + I_2(g)$ $\Delta H = 305.06$ kJ

Add eq. (iii) and eq. (v)

(*vi*) $Cl_2(g) + I_2(s) \longrightarrow 2Cl(g) + 2I(g)$ $\Delta H = 456.16$ kJ

Divide eq. (*vi*) by 2

(*vii*) $$\frac{1}{2}Cl_2(g) + \frac{1}{2}I_2(s) \longrightarrow Cl(g) + I(g) \qquad \Delta H = 228.08 \text{ kJ}$$

Subtract eq. (*iv*)

$ICl(g) \longrightarrow I(g) + Cl(g)$ $\Delta H = 211.3$ kJ

$$\frac{1}{2}Cl_2(g) + \frac{1}{2}I_2(s) \longrightarrow ICl(g) \qquad \Delta H = 16.78 \text{ kJ}$$

A32. (*c*) Freezing is an exothermic process. Therefore, the heat released increases the entropy of the surroundings.

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A34. (*d*) $\Delta G^\circ = -RT \log K$

$$\frac{\Delta G^\circ}{RT} = -2.303 \log K$$

A41.(*b*) For adiabatic process, $q = 0$ and therefore, ΔS (sys) = 0.
Irrevesible process is accompanied by increase of entropy and therefore, ΔS (surr) = +ve.

A42. (*d*) The reaction is at equilibrium so that $\Delta H = T\Delta S$

A44. (*c*) For a spontaneous reaction,
ΔG = (–ve), ΔS = + ve and ΔH = + ve and $T\Delta S > \Delta H$

A45.(*d*) :
$$\Delta G = \Delta H - T\Delta S$$
$$0 = \Delta H - T\Delta S$$
$$T\Delta S = \Delta H$$
$$T = \frac{\Delta H}{\Delta S} = \frac{30{,}000 \text{J mol}^{-1}}{105 \text{ JK}^{-1} \text{ mol}^{-1}} = 285.7\text{K}$$

A46. (*a*) : For a spontaneous reaction,
ΔH = – ve, K > 1 and E°_{cell} = + ve

B. *mcq from competitive examinations*

B1. (*b*) : Enthalpy of formation of $H_2O(l)$ is

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(l)$$
$$\therefore \Delta H = -x_2 \text{ kJ mol}^{-1}$$

B2. (*d*) : $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow HCl$

$$\Delta H = \frac{1}{2}\text{B.E.(H—H)} + \frac{1}{2}\text{B.E. (Cl—Cl)} - \text{B.E. (H—Cl)}$$
$$-90 = \frac{1}{2}(430) + \frac{1}{2}(240) - \text{B.E. (H—Cl)}$$
$$\therefore \text{B.E. (H—Cl)} = 215 + 120 + 90 = \mathbf{425 \text{ kJ mol}^{-1}}$$

B3. (*d*) : Energy consumed for walking a distance of 5km
= 150 × 5 = 750 kJ
Energy provided by 1 mol of glucose = 3000 kJ

$$\text{Actual energy provided} = 3000 \times \frac{30}{100}$$
= 900 kJ
900 kJ of energy require glucose = 180 g

$$750 \text{ kJ of energy require glucose} = \frac{180 \times 750}{900}$$
$$= \mathbf{150 \text{ g}}$$

B4. (*c*) : Solid ice (–10°C) $\xrightarrow{\Delta H_1}$ Solid ice (0°C) $\xrightarrow{\Delta H_2}$ Liquid water (0°C) $\xrightarrow{\Delta H_3}$ Liquid water (10°C)

$$n = \frac{10}{18} \text{ mol}$$
$$\Delta H_1 = nC_p[H_2O(s)]\Delta T$$
$$= \frac{10}{18} \times 37.8 \times 10 = 210$$
$$\Delta H_2 = n\Delta_{fus}H^\circ$$
$$= \frac{10}{18} \times 6012 = 3340$$
$$\Delta H_3 = nC_p[H_2O(l)]\,\Delta T$$
$$= \frac{10}{18} \times 75.6 \times 10 = 420$$
$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$
$$= 210 + 3340 + 420 = \mathbf{3970 \text{ J}}$$

B6. (*c*) : For a process to be spontaneous $\Delta S_{universe}$ must be positive. Here,
$$\Delta S_{universe} = -22.13 + 22.05 = \mathbf{-0.08 \text{ kJ}}$$

B7. (*a*) : $PH_3(g) \longrightarrow P(g) + 3H(g)$ $\Delta_r H^\circ = \mathbf{954 \text{ kJ mol}^{-1}}$
The bond energy is the average energy for 3 P—H bonds as :
Average bond energy of P—H bond
$$= \frac{954}{3} = 318 \text{ kJ mol}^{-1}$$
P_2H_4 has four P—H bonds and one P—P bond
$$\text{B.E (P—P)} + 4 \text{ B.E (P—H)} = 1485 \text{ kJ mol}^{-1}$$
$$\text{B.E (P—P)} + 4 \times 318 = 1485 \text{ kJ mol}^{-1}$$
$$\text{B.E (P—P)} = 1485 - 4 \times 318$$
$$= 1485 - 1272$$
$$= \mathbf{213 \text{ kJ mol}^{-1}}$$

B8. (*b*) : For a spontaneous process, ΔG must be negative.
Here, ΔG will be negative when $T\Delta S > \Delta H$
ΔH = 170 kJ = 170000 J
ΔS = 170 J/K/mol

$$T\Delta S > \Delta H \text{ only when } T = \frac{\Delta H}{\Delta S} = \frac{170000}{170} = 1000 \text{ K.}$$
i.e. greater than 1000 K or 1110 K.

B9. (*b*) :
$$\Delta_f H = \text{B.E.}_{\text{reactants}} - \text{B.E}_{\text{products}}$$
$$= [\text{B.E.}_{(C=C)} + \text{B.E.}_{(H—H)} + 4 \times \text{B.E.}_{(C—H)}] - [\text{B.E.}_{(C—C)} + 6 \times \text{B.E.}_{(C—H)}]$$
$$= (606.10 + 431.37 + 4 \times 410.5) - (336.49 + 6 \times 410.50)$$
$$= \mathbf{-120.02 \text{ kJ mol}^{-1}.}$$

B10. (*b*) :
$$\Delta S^\circ = S^\circ(XY_3) - \frac{1}{2}S^\circ(X_2) - \frac{3}{2}S^\circ(Y_2)$$
$$= 50 - \frac{1}{2}(60) - \frac{3}{2}(40) = -40 \text{ JK}^{-1} \text{ mol}^{-1}$$
$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-30 \times 10^3 \text{ J mol}^{-1}}{-40 \text{ JK}^{-1} \text{ mol}^{-1}} = \mathbf{750 \text{ K}}$$

B11. (*c*) :
$$\Delta E = C \times \Delta t \times \frac{M}{m}$$
$$= 30 \text{ kJ K}^{-1} \times 4 \times \frac{12}{4}$$
$$= 360 \text{ kJ mol}^{-1}$$
$$\Delta E = \mathbf{-360 \text{ kJ mol}^{-1}}$$

B12. (*c*) :
$4H(g) \longrightarrow 2H_2(g)$ $\Delta H = -869.6$ kJ
$2H_2(g) \longrightarrow 4H(g)$ $\Delta H = 869.6$ kJ
$H_2(g) \longrightarrow 2H(g)$ $\Delta H = 44.8$ kJ

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B13. (*c*) : For free expansion of an ideal gas under adiabatic conditions : $q = 0$, $\Delta T = 0$, $w = 0$

B14. (*c*) : ΔS is negative because there is decrease in gaseous moles (Δn_g = – ve).

B15. (*a*) : $H_2O(l) \longrightarrow H_2O(g)$

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta n_g = 1$, $\Delta H = 40.66 \times 10^3$ J mol^{-1},

$T = 373$ K

$40660 = \Delta U + 1 \times 8.314 \times 373$

$\Delta U = 40660 - 3101.12$

$= \mathbf{37.56\ kJ\ mol^{-1}}$

B16. (*a*) : $C(gr) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

Since $\Delta n_g = 1 - \frac{1}{2} = +ve$

$\Delta S = +ve$

$\Delta G = \Delta H - T\Delta S$

Since ΔS is +ve, increase in temperature will make $T\Delta S$ more negative and ΔG will decrease with increasing temperature.

B17. (*a*) : $\Delta S = \frac{\Delta H}{T_m} = \frac{1.435 \times 1000}{273} = 5.26$ cal/mol K

B18. (*a*) : (*i*) $4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g)$, $\Delta H = -110$ kJ

Given that,

(*ii*) $N_2O_5(s) \longrightarrow N_2O_5(g)$, $\Delta H = 53$ kJ mol^{-1}

(*iii*) $2N_2O_5(s) \longrightarrow 2N_2O_5(g)$, $\Delta H = 106$ kJ mol^{-1}

Subtracting eq. (*iii*) from (*i*),

$4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(s)$

then $\Delta H = -110 - 106 = \mathbf{-216\ kJ\ mol^{-1}}$

B19. (*b*) : $X_2O_4(l) \longrightarrow 2XO_2(g)$

$\Delta U = 2.1$ kcal $= 2100$ cal; $\Delta S = 20$ cal K^{-1}

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta n_g = 2 - 0 = 2$; $R = 2$ cal K^{-1} mol^{-1}; $T = 300$ K

$\Delta H = 2100 + (2 \times 2 \times 300) = 3300$ cal

$\Delta G = \Delta H - T\Delta S = 3300 - 300(20) = -2700$ cal

$= \mathbf{-2.7\ kcal}$

B20. (*c*) : $CuSO_4 \cdot 5H_2O(s) + aq \longrightarrow CuSO_4(aq)$

$\Delta H_1 = 11.7$ kJ mol^{-1}

$CuSO_4(s) + aq \longrightarrow CuSO_4(aq)$

$\Delta H_2 = -65.5$ kJ mol^{-1}

$CuSO_4(s) + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O(s)$

$\Delta H_3 = ?$

$\Delta H_2 = \Delta H_3 + \Delta H_1$

or $\Delta H_3 = \Delta H_2 - \Delta H_1$

$= -65.5 - (11.7)$

$= -77.2$ kJ mol^{-1}

B21. (*a*) : $\Delta_f H^\circ = -91.8$ kJ mol^{-1}

Heat required to decompose 1 mol or 17 g of NH_3 $= 91.8$ kJ

Heat required to decompose 34 g of NH_3

$= \frac{91.8}{17} \times 34 = 183.6$ kJ

B22. (*b*) : For isothermal reversible expansion of an ideal gas

$$w = -2.303\ nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times \frac{16}{32} \times 8.314 \times 300 \log \frac{25}{2.5}$$

$$= -2872.07\ J$$

or $= \frac{-2872.07}{101.3} = -28.35$ L atm

$\therefore$ Work done by the system = 28.35 L atm

B23. (*c*) : Heat of combustion of carbon to CO_2

= Heat of formation of CO_2

$= -393.5$ kJ mol

Heat released for forming 1 mol (44g) of $CO_2 = -393.5$ kJ

Heat released for formation of 35.2 g of

$CO_2 = \frac{-393.5 \times 35.2}{44}$

$= -314.8$

or $= -315$ kJ

B24. (*a*) : $\Delta G = \Delta G^\circ + 2.303\ RT \log K$

At equilibrium, $\Delta G = 0$

$\therefore \quad 0 = \Delta G^\circ + 2.303\ RT \log K$

or $\Delta G^\circ = -2.303\ RT \log K$

B26. (*b*) : For an ideal gas undergoing reversible expansion, when temperature changes from T_i to T_f and pressure changes from p_i to p_f,

$$\Delta S = n\ C_p\ ln \left(\frac{T_f}{T_i}\right) + n\ R\ ln \left(\frac{p_i}{p_f}\right)$$

Since the process is isothermal, $T_i = T_f$ and $ln\ 1 = 0$

$$\therefore \quad \Delta S = n\ R\ ln \left(\frac{p_i}{p_f}\right)$$

B27. (*a*) : $\Delta G = \Delta H - T\Delta S$

For a reaction to be at equilibrium,

$\Delta G = 0$

$\Delta H = T\Delta S$

or $T = \frac{\Delta H}{\Delta S} = \frac{35.5 \times 10^3}{83.6}$

$= \mathbf{425\ K}$

Since reaction is endothermic, it will be spontaneous at $T > 425$ K.

B28. (*b*) : $\Delta U = q + w$

For adiabatic process, $q = 0$

$\Delta U = -w = -p\Delta V$

$= -2.5$ atm $(4.5 - 2.5)$ L

$= -5$ L atm $= -5 \times 101.3$ J $= \mathbf{-506.5\ J}$

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B29. (*c*) : Let bond dissociation energy of X_2 be x kJ mol^{-1}. Then,

B.E. of $Y_2 = 0.5x$ kJ mol^{-1}

B.E. of XY = x kJ mol^{-1}

$$\frac{1}{2}X_2 + \frac{1}{2}Y_2 \longrightarrow XY \quad \Delta H = -200 \text{ kJ mol}^{-1}$$

$\Delta H = \Sigma$B.E. (reactants) – ΣB.E. (products)

$$\Delta H = \frac{1}{2}\text{B.E.}(X_2) + \frac{1}{2}\text{B.E.}(Y_2) - \text{B.E.}(XY)$$

$$-200 = \frac{1}{2}(x) + \frac{1}{2}(0.5x) - 1(x)$$

$$-200 = -0.25x$$

$$\therefore x = \frac{200}{0.25} = \mathbf{800\ kJ\ mol^{-1}}$$

B30. (*b*) : $H_2O(l) \longrightarrow H_2O(g)$

$\Delta G = 41$ kJ mol^{-1}

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta n_g = 1$

$41 = \Delta U + 1 \times 8.3 \times 10^{-3} \times 373$

$41 = \Delta U + 3.096$

$\Delta U = 41 - 3.096 = \text{mol}^{-1}$

37.904 kJ

B31. (*c*) : $T = \dfrac{\Delta H^\circ}{\Delta S^\circ} = \dfrac{179.1 \times 10^3 \text{ J}}{160.0 \text{ JK}^{-1}}$

$= 1117.97 \approx$ **1118 K.**

B32. (*d*) : Equation (*i*) – (*ii*) gives

$S(Rh) + O_2(g) \longrightarrow SO_2(g)$;

$\Delta_f H = \Delta H_1 - \Delta H_2$

$= -2x + y$

B33. (*c*) : For the process :

$$\frac{1}{2}Cl_2(g) \longrightarrow Cl^-(aq)$$

$$\Delta H = \frac{1}{2}\Delta_{diss}H(Cl_2) + \Delta_{eg}H(Cl) + \Delta_{hyd}H(Cl^-)$$

$$= \frac{240}{2} + (-349) + (-381) = -610 \text{ kJ mol}^{-1}$$

B34. (*d*) : $CH_3OH(l) + \dfrac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$\Delta_f H = -726$ kJ mol^{-1}

$\Delta_r G = \Delta_f G_{(\text{products})} - \Sigma\Delta_f G_{(\text{reactants})}$

$= \left[\Delta_f G_{CO_2} + 2 \times \Delta_f G_{H_2O}\right]$

$\quad - \left[\Delta_f G_{(CH_3OH)} + \dfrac{3}{2}\Delta_f G_{(O_2)}\right]$

$= [-394.4 + 2 \times (-237.2)] -$

$\quad [-166.2 + \dfrac{3}{2}(0)]$

$= -702.6$ kJ mol^{-1}.

% Efficiency

$$= \frac{\Delta_f G}{\Delta_f H} \times 100 = \frac{-702.6}{-723} \times 100$$

$= 96.77\% \approx$ **97%**

B35. (*b*) : $H_2(g) + \dfrac{1}{2}O_2(g) \longrightarrow H^+(aq) + OH^-(aq)$, $\Delta H_1 = ?$

$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$

$\Delta H_2 = 57.32$ kJ ...(*i*)

$H_2(g) + \dfrac{1}{2}O_2(g) \longrightarrow H_2O(l)$

$\Delta H_3 = -286.2$ kJ ...(*ii*)

ΔH_1 will be obtained by adding (*i*) and (*ii*)

$= 57.32 + (-286.2) =$ **–228.88 kJ**

B36. (*d*) : The required equation is

(*i*) $NH_3(g) \longrightarrow N(g) + 3H(g)$

The given equations are

(*ii*) $\dfrac{1}{2}N_2(g) + \dfrac{3}{2}H_2(g) \longrightarrow NH_3(g) \quad \Delta H = -46$ kJ

(*iii*) $2H(g) \longrightarrow H_2(g) \quad \Delta H = -436$ kJ

(*iv*) $2N(g) \longrightarrow N_2(g) \quad \Delta H = -712$ kJ

Multiplying eq. (*iv*) by $\dfrac{1}{2}$ and eq. (*iii*) by $\dfrac{3}{2}$ and adding

(*v*) $N(g) + 3H(g) \longrightarrow \dfrac{1}{2}N_2(g) + \dfrac{3}{2}H_2(g)$

$\Delta H = -1010$ kJ

Adding eq. (*ii*) and (*v*)

$N(g) + 3H(g) \longrightarrow NH_3(g) \quad \Delta H = -1056$ kJ

or $NH_3(g) \longrightarrow N(g) + 3H(g) \quad \Delta H = 1056$ kJ

This gives enthalpy of dissociation of 3 N – H bonds

$\therefore$ Average bond enthalpy of N – H $= \dfrac{1056}{3}$

= 352 kJ

B37. (*d*) : $\Delta G = \Delta H - T\Delta S$

At equilibrium, $\Delta G = 0$

$0 = \Delta H - T\Delta S$

or $T_e\Delta S = \Delta H$

$$T_e = \frac{\Delta H}{\Delta S}$$

Since it is an endothermic reaction, it is favoured by high temperature so that $T > T_e$.

B38. (*b*) : $w = -2.303\ nRT \log\dfrac{V_2}{V_1}$

$= -2.303 \times 1 \times 8.314 \times 300 \log\dfrac{20}{10}$

$= -1728$ J

$\therefore$ Work done = **1728 J**

B39. (*c*) : $Q = nC\Delta T$

$n = \dfrac{54}{27} = 2$ mol,

$\Delta T = 50 - 30 = 20°$

$Q = 2 \text{ mol} \times 25 \text{ JK}^{-1}\text{mol}^{-1} \times 20 \text{ K}$

$= 1000$ J = **1.0 kJ**

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B40. (*a*) : $\Delta S = 2.303\ nR\ \log\frac{V_2}{V_1}$

$= 2.303 \times 2 \times 8.314 \log\frac{100}{10}$

$= 2.303 \times 2 \times 8.314 \times 1$

$= \mathbf{38.3\ J\ mol^{-1}\ K^{-1}}$

B41. (*b*) : $\Delta H = \Delta U + \Delta n_g\ RT$

$\Delta U = \Delta H - \Delta n_g\ RT$

$\Delta n_g = 2 - 3 = -1$

$\Delta U = -1366.5 - (-1) \times 8.314 \times 10^{-3} \times 300$

$= -1366.5 + 2.494$

$= \mathbf{-1364.0}$

B42. (*b*) : (*i*) $C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6\ CO_2(g) + 3H_2O(l)$

$\Delta H = -3270\ kJ\ mol^{-1}$

(*ii*) $C(gr) + O_2(g) \longrightarrow CO_2(g)$

$\Delta H = -394\ kJ\ mol^{-1}$

(*iii*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$

$\Delta H = -286\ kJ\ mol^{-1}$

The required equation is

(*iv*) $6C\ (gr) + 3H_2(g) \rightarrow C_6H_6(l)$; $\Delta H = ?$

Multiply eq.(*ii*) by 6 and eq (*iii*) by 3 and adding, we get :

(*v*) $6C(gr) + \frac{15}{2}O_2(g) + 3H_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$; $\Delta H = -3222 kJ$

Subtract eq(*i*) from eq (*v*)

$6\ C(gr) + 3H_2(g) \longrightarrow C_6H_6(l)$ $\Delta H = \mathbf{+48\ kJ\ mol^{-1}}$.

B43. (*b*) : is incorrect because

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$-RT \ln K = \Delta H^\circ - T\Delta S^\circ$

$\therefore \quad \ln K = -\frac{\Delta H^\circ - T\Delta S}{RT}$

B44. (*d*) : For isothermal process, $\Delta T = 0$

$\Delta U = nC_v\ \Delta T = 0$

$\Delta H = nC_P\ \Delta T = 0$

According to first law of thermodynamics

$\Delta U = q + w$

Since $\Delta U = 0,\ q \neq w \neq 0$

B45. (*c*) : (*i*) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$

$\Delta H = -1415 kJ$

(*ii*) $C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

$\Delta H = -1566\ kJ$

(*iii*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H = -286\ kJ$

Adding eq. (*i*) and (*iii*)

$C_2H_4(g) + \frac{7}{2}O_2(g) + H_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

$\Delta H = -1701\ kJ$

Subtracting eqn (*ii*) from eqn (*iv*)

$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$ $\Delta H = -135\ kJ$

B46. (*b*) : Since it absorbs heat, $q = +208$ K

Since the process is isothermal, $\Delta U = 0$

From first law of thermodynamics,

$\Delta U = q + w$

$0 = 208 + w$ or $w = \mathbf{-208\ J}$

B47. (*b*) : $\Delta H_{vap} = 24.64\ kJ\ mol^{-1} = 24640\ J\ mol^{-1}$

Boiling point, T = 35°C = 308 K

$\Delta S = \frac{\Delta H}{T} = \frac{24640}{308} = \mathbf{80\ J\ K^{-1}\ mol^{-1}}$

B48. (*b*) : $\Delta H = n \times C_p \times \Delta T$

$= 2 \times \frac{5}{2} R \times (125 - 225) = \mathbf{-500\ R}$

B49. (*a*) : $C + \frac{1}{2}O_2 \longrightarrow CO \qquad \Delta H = ?$

(*i*) $C + O_2 \longrightarrow CO_2 \qquad \Delta H_1 = -x\ kJ$

(*ii*) $2CO + O_2 \longrightarrow 2CO_2 \qquad \Delta H_2 = -y\ kJ$

$\Delta H = \Delta H_1 - \frac{1}{2}\Delta H_2$

$= -x - \left(\frac{1}{2}(-y)\right) = \frac{y}{2} - x = \frac{y - 2x}{2}$

B50. (*a*) : Entropy of vaporisation = 58 J K^{-1} mol^{-1}

Entropy of condensation = − 58 J K^{-1} mol^{-1}

$\therefore$ Entropy of condensation for 1 mol (58g) = − 58 J K^{-1} mol^{-1}

$\therefore$ Entropy of condensation for 100 g

$= \frac{-58}{58} \times 100$

$= \mathbf{-100\ J\ K^{-1}\ mol^{-1}}$

B51. (*b*) : 1kg of coke = $\frac{1000}{12}$ = 83.33 mol

$C + O_2 \longrightarrow CO_2$

Heat liberated by burning 83.33 mol of coke = 83.33 × 393.5 kJ

$\underbrace{CO + H_2}_{\text{Water gas}} + O_2 \longrightarrow CO_2 + H_2O$

Heat liberated by burning 1 mol of water gas = 285 + 285 = 570 kJ

Heat liberated by burning water gas obtained from 1 kg of coke

$= 83.33 \times 570$ kJ

Ratio of heat liberated

Coke : water gas

$83.33 \times 393.5 : 83.33 \times 570$

$393.5 : 570$

$0.69 : 1$

B52. (*b*) : $\Delta H = \Delta U + \Delta n_g\ RT$

$\Delta n_g = 6 - \frac{7}{2} = 2.5$

$\Delta U = \Delta H - \Delta n_g\ RT$

$= -780\ 980 - (2.5) \times 2 \times 298$

$= -782470$ cal

or $= \mathbf{-782.470\ kcal}$

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B53. (*b*) : In a bomb calorimeter, volume is constant. Heat released at constant volume = $\Delta U = -1364.47$ kJ

$R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}

$\Delta n_g = 2 - 3 = -1$

$\Delta H = \Delta U + \Delta n_g RT$

$= -1364.47 + (-1)(8.314 \times 10^{-3})(298)$

$=$ **-1366.95 kJ mol^{-1}**

B54. (*c*) : $\Delta H = \Delta U + \Delta n_g RT$

$X_2Y_4(l) \longrightarrow 2XY_2(g)$

$\Delta n_g = 2 - 0 = 2$, $R = 2$ cal K^{-1} mol^{-1}

$\Delta H = 2200 + 2 \times 2 \times 300$

$= 3400$ cal

$\Delta G = \Delta H - T\Delta S = 3400 - (300 \times 20)$

$=$ **-2800 cal**

B55. (*b*) : $C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

1 mol $\frac{7}{2}$ mol 2 mol 3 mol

Moles of ethane $= \frac{0.090 \times 10^3}{30} = 3$ mol

$\Delta n_g = 2 - \left(1 + \frac{7}{2}\right) = -\frac{5}{2}$

$w = -p\Delta V = -\Delta n_g nRT$

$= -\left(-\frac{5}{2}\right) \times 3 \times 8.314 \times 300$

$=$ **18.706 kJ**

B56. (*a*) : $w = p_{ext}(V_2 - V_1)$

$p_{ext} = 100\ kP = 10^5$ Pa

$\therefore \quad w = 10^5 \text{Pa}\ (1 - 0.001)\text{m}^3$

$= 10^5 \times 99.9 \times 10^{-2}$ Pa m^3

$= 99.9 \times 10^3$ J ($\because$ Pa m^3 = J)

$=$ **99.9 kJ**

B57. (*d*) : $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

Work done, $w = -p\Delta V = -\Delta n_g RT$

$\Delta n_g = 1 - 3 = -2$, $T = 300$K

$w = -(-2 \times 8.314 \times 300)$

$= 4988.4$ J

For 0.5 mol of CH_4

$w = \frac{4988.4}{2} =$ **2494.2**

B58. (*e*) : $Fe_2O_3(s) + 3H_2(g) \longrightarrow 3H_2O(l) + 2Fe(s)$

$\Delta_r H^\circ = [3\Delta_f H^\circ(H_2O) + 2\Delta_f H^\circ(Fe)] - [\Delta_f H^\circ(Fe_2O_3) + 3\Delta_f H^\circ(H_2)]$

$= 3 \times (-286) + 2(0) - (-824) - 3(0)$

$= -858 + 824 =$ **-34 kJ mol^{-1}**

B59. (*b*) : From the K_a values, strength of acids is in the order:

HF(X) > HCOOH(Y) > CH_3COOH (W) > HCN(Z)

Stronger the acid, higher is the heat liberated during the neutralisation because lesser energy is required for ionisation. Therefore, correct order of heat liberated is X > Y > W > Z.

B60. (*d*) : $\Delta_r H = \Sigma BE$ (reactants) $- \Sigma BE$ (products)

$= BE(H_2) + BE(Br_2) - 2BE(HBr)$

$= 433 + 192 - 2 \times 364$

$=$ **-103 kJ**

B62. (*d*) : (*i*) $C(s) + O_2(g) \longrightarrow CO_2(g)$

$\Delta H = -393.5$ kJ mol^{-1}

(*ii*) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$

$\Delta H = -283.5$ kJ mol^{-1}

Subtracting equation (*ii*) from equation (*i*)

$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) =$ **-110.0 kJ mol^{-1}**

B65. (*c*) : (*i*) $C_{(graphite)} + O_2 \longrightarrow CO_2(g)$

$\Delta H^\circ = -393.5$ kJ mol^{-1}

(*ii*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$

$\Delta H^\circ = -285.8$ kJ mol^{-1}

(*iii*) $CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g)$

$\Delta H = 890.3$ kJ mol^{-1}

The required equation is

(*iv*) $C_{(graphite)} + 2H_2(g) \longrightarrow CH_4(g)\ \Delta H^\circ = ?$

By applying eq.(*i*) + 2 × eq.(*ii*) + eq.(*iii*)

$\Delta H^\circ = -393.5 + 2(-285.8) + 890.3 =$ **-74.8 kJ mol^{-1}**

B66. (*c*) : For adiabatic process, $q = 0$

$\Delta U = q + w$ or $\Delta U = w$

B67. (*a*) : $\Delta H = -560$ kcal, $\Delta U = ?$

$C_8H_{16}(l) + 12\ O_2(g) \longrightarrow 8CO_2(g) + 8H_2O(l)$

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta n_g = 8 - 12 = -4$

$-560000 = \Delta U + (-4) \times 2 \times 300$

$\Delta U = -560000 + 2400$

$=$ **-557600**

B68. (*a*) : For a reaction to be spontaneous, ΔG should be –ve.

$\Delta G = \Delta H - T\Delta S$

Given that ΔH = – ve, ΔS = – ve

$\Delta G = (-) - T(-)$

ΔG will be – ve only at low temperature

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B69. (*b*) : $\Delta S = 2.303\ nR \log \frac{V_f}{V_i}$

$\Delta S = 2.303 \times 1 \times 2 \log \frac{6}{3}$

$= 2.303 \times 1 \times 2 \times 0.3010 = 1.386\ cal\ K^{-1}$

B70. (*a*) : 0.25 mol of NaOH will react with 0.25 mol of HCl to form water. Heat released for neutralisation of 0.25 mol of NaOH with HCl

$= 0.25 \times 13.7 =$ **3.425 kcal**

B71. (*a*) : According to the problem,

$P \propto T^3$ or $P = kT^3$ or $PT^{-3} = k$ ... (*i*)

For a reversible adiabatic process,

$T^{\gamma} P^{1-\gamma} = k$

$T^{\frac{\gamma}{1-\gamma}} P = k$ ... (*ii*)

Comparing eq. (*i*) and (*ii*)

$\frac{\gamma}{1-\gamma} = -3$ or $\gamma = -3 + 3\gamma$

or $-2\gamma = -3$ or $\gamma = 3/2$

B72. (*b*) : $2C(s) + \frac{1}{2}O_2(g) + 3H_2(g) \longrightarrow C_2H_5OH\ (l)$

$\Delta_f H = -277.7 kJ\ mol^{-1}$

Doubling the equation,

$4C(s) + O_2(g) + 6H_2(g) \longrightarrow 2C_2H_5OH\ (l)$

$\Delta H = 2 \times (-277.7) =$ **– 555.4 kJ mol^{-1}**

B75. (*d*) : $C_6H_6(l) + \frac{15}{2} O_2(g) \longrightarrow 6CO_2(g) + 3H_2O\ (l)$

$\Delta n_g = 6 - \frac{15}{2} = -\frac{3}{2}$

$\Delta H = \Delta U + \Delta n_g\ RT$

$= -3263.9 + \left(\frac{-3}{2}\right) \times 8.314 \times 10^{-3} \times 298$

$= -3263.9 - 3.716$

$=$ **– 3267.676**

B76. (*c*) : (*i*) = (*ii*) + (*iii*)

$\therefore \quad x = y + z$

B77. (*c*) : For isothermal expansion,

$PV_m =$ Constant $= K$ [graph(*c*)]

or $P = \frac{K}{V_m}$ [graph (*a*)]

B78. (*b*) : $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

Decrease in number of gaseous molecules

B81. (*b*) : $\Delta S(A \to B) = \Delta S(A \to C) + \Delta S(C \to D) + \Delta S(D \to B)$

$= \Delta S(A \to C) + \Delta S(C \to D) - \Delta S(B \to D)$

$= 50 + 30 - (20) =$ **60 eV**

B82. (*a*) : This is a phase transformation and hence $\Delta G = 0$. Since $H_2O\ (l)$ is changing to $H_2O\ (g)$ at the same temperature and pressure, ΔS = +ve.

B83. (*b*) : $Cl_2\ (g)$ in elemental state.

B84. (*d*) : The given equations are

(*i*) $2C(g) + H_2(g) \longrightarrow C_2H_2(g)$ $\Delta H_1 = 225\ kJ\ mol^{-1}$

(*ii*) $2C(s) \longrightarrow 2C(g)$ $\Delta H_2 = 1410\ kJ\ mol^{-1}$

(*iii*) $H_2(g) \longrightarrow 2H(g)$ $\Delta H_3 = 330\ kJ\ mol^{-1}$

Ethyne molecule breaks as

(*iv*) $C_2H_2(g) \longrightarrow 2C(g) + 2H(g)$ $\Delta H = ?$

Eq. (*iv*) can be obtained by adding eq. (*ii*) and (*iii*) and then subtracting eq. (*i*)

$\therefore \quad \Delta H = \Delta H_2 + \Delta H_3 - \Delta H_1$

$= 1410 + 330 - 225 = 1515\ kJ\ mol^{-1}$

Eq.(*iv*) involves breaking of one C≡C bond and two C – H bonds.

$\therefore \quad \Delta H = 2 \times$ B.E. (C – H) + B.E. (C ≡ C)

$1515 = 2 \times 350 +$ B.E. (C ≡ C)

$\therefore$ B.E. (C ≡ C) $= 1515 - 700$

$=$ **815 kJ mol^{-1}**

B85. (*c*) : $C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$

$\Delta H^\circ_{comb} = \sum \Delta H^\circ_f$ (products) $- \sum \Delta H^\circ_f$ (reactants)

$\left[6 \times \Delta H^\circ_f(CO_2) + 6\Delta H^\circ_f(H_2O)\right]$

$- \left[\Delta H^\circ_f(C_6H_{12}O_6) + 6\Delta H^\circ_f(O_2)\right]$

$= [6 \times (-400) + 6(-300)] - [-1300 + 6(0)]$

$= -2400 - 1800 + 1300 = -2900\ kJ\ mol^{-1}$

Standard enthalpy of combustion per gram $= \frac{-2900}{180}$

$= -16.11\ kJg^{-1}$

B86. (*b*) : $H_2O(l) \longrightarrow H_2O(g)$

For this reaction, ΔS total = 0

$\Delta S_{system} + \Delta S_{surroundings} = 0$

$\therefore \quad \Delta S_{system} = -\Delta S_{surroundings}$

$\therefore \quad \Delta S_{system} > 0$ and $\Delta S_{surroundings} < 0$

B87. (*c*) : For isothermal expansion, $\Delta U = 0$

Since pressure is constant, process is irreversible

$q_{irrev} = -w_{irrev} = -(-p\ \Delta V)$

$= -[-3(2 - 1)] = 3$ L atm

$= 3 \times 101.3$ J

$\Delta S_{surr} = \frac{-q_{irrev}}{T} = -\frac{3 \times 101.3\ J}{300\ K}$

$=$ **–1.013 JK^{-1}**

B88. (*c*) : C (graphite) $\longrightarrow$ C(diamond)

$\Delta G^\circ = \Delta_f G^\circ$ (diamond) $- \Delta_f G^\circ$(graphite)

$\Delta G^\circ = 2.9 - 0 = 2.9\ kJ\ mol^{-1} = 2900\ J\ mol^{-1}$

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$\Delta V = 2 \times 10^{-6}\ m^3\ mol^{-1}$

$\Delta G^\circ = \Delta V.\Delta p$

$2900\ J\ mol^{-1} = (2 \times 10^{-6}\ m^3\ mol^{-1})\ (p_e - 1)$

$$p_e - 1 = \frac{2900}{2\times10^{-6}} = 1450\times10^6$$

$$\text{or } p_e - 1 = \frac{1450\times10^6}{10^5} = 14500 \text{ bar}$$

$$p_e = 14500 + 1 = \mathbf{14501\ bar}$$

C. *mcq with more than one correct answer*

C8. (*a, c*) : Since ΔS is a state function, it depends only on the initial and final states, so that

$\Delta S_{X\to Z} = \Delta S_{X\to Y} + \Delta S_{Y\to Z}$

Now $\Delta S_{Y\to Z}$ = is not zero, therefore,

$\Delta S_{X-Y\to Z} \neq \Delta S_{X\to Y}$

Since work is not a state function and therefore, it depends on path.

$w_{X\to Z} \neq w_{X\to Y} + w_{Y\to Z}$

$w_{X\to Y} = pdV$ (p is constant)

$w_{Y\to Z} = 0$ (V is constant)

$$w_{X\to Z} = 2.303\ nRT\ \log\frac{V_2}{V_1}$$

$w_{X\to Y\to Z} = w_{X\to Y} + w_{Y\to Z}$

As $w_{Y\to Z} = 0,\ w_{X\to Y\to Z} = w_{X\to Y}$

C9. (*a, c, d*): For isothermal expansion,

$\Delta T = 0$ *i.e.*, $T_1 = T_2$

Hence, (*a*) is correct.

(*c*) $W_{isothermal} > W_{adiabatic}$ because area under the isothermal curve is greater than under the adiabatic curve. Hence, (*c*) is correct.

(*d*) $\Delta U_{adiabatic}$ = –ve because during adiabatic expansion, internal energy decreases. Thus $\Delta U_{isothermal} > \Delta U_{adiabatic}$. Hence, (*d*) is correct.

(*b*) $T_3 < T_1$ because cooling takes place on adiabatic expansion. Hence, (*b*) is not correct.

C10. (*b, c, d*): For an ideal solution,

(*a*) $\Delta G < 0$ for mixing. Hence (*a*) is not correct.

(*b*) ΔS_{system} is +ve because disorder increases

(*c*) $\Delta S_{surr} = 0$ because no heat is exchanged in case of ideal solution.

(*d*) $\Delta H_{mix} = 0$ for an ideal solution.

C12. (*a,b,c*): Since the gas is thermally insulated, $q = 0$

Also, $p_{ext} = 0$, hence $w = 0$

From first law of thermodynamics,

$\Delta U = q + w = 0$

$\therefore \quad \Delta T = 0$ or $T_2 = T_1$

Applying ideal gas equation,

$pV = nRT$

As T is constant

$p_1V_1 = p_2V_2$

Equation pV^γ = constant is applicable only for the ideal gas in reversible adiabatic process. Hence, the relation

$p_2V_2^\gamma = p_1V_1^\gamma$ is not applicable.

C15. (*b,c*): (*a*) q_{AC} (isochoric) = $\Delta U_{AC} = nC_v(T_2 - T_1)$ = ΔU_{BC} (isobaric)

$$w_{AB}\ (\text{isothermal}) = -n\ RT\ \ln\frac{V_2}{V_1}$$

So, (*a*) is not correct

(*b*) w_{BC} (isobaric) = $-P_2(V_1 - V_2) = P_2(V_2 - V_1)$

and q_{BC} (isobaric) = $q + w = n\ C_v(T_2 - T_1) + P_2(V_1 - V_2) + [-P_2(V_1 - V_2)]$

$= nC_v(T_2 - T_1) = \Delta H_{AC}$ (isochoric)

So, (*b*) is correct.

(*c*) ΔH_{CA} (isochoric) = $nC_p(T_1 - T_2)$

ΔU_{CA} (isochoric) = $nC_v(T_1 - T_2)$

$\Delta H_{CA} < \Delta U_{CA}$ both are negative and $T_1 < T_2$

q_{AC} (isochoric) = $nC_V(T_2 - T_1) = \Delta U_{BC}$ (isobaric)

So, (*c*) is correct.

(*d*) q_{BC} (isochoric) = $q+w = nC_V(T_2 - T_1) + P_2(V_1 - V_2) + [(-P_2(V_1 - V_2)]$

$= nC_V(T_2 - T_1) = \Delta H_{AC}$ (isobaric)

$\Delta H_{CA} < \Delta U_{CA}$

So, (*d*) is not correct

D. *mcq based on comprehension*

D7. (*b*) For isochoric process, volume remains constant. L ⟶ M and N ⟶ K are having constant volume and therefore, these processes are isochoric.

D8. (*c*) K ⟶ L volume increases at constant P

$\therefore$ Temperature increases, hence heating

L ⟶ M constant V but pressure decreases

$\therefore$ Temperature decreases, hence cooling

M ⟶ N constant P but volume decreases

$\therefore$ Temperature decreases, hence cooling

N ⟶ K constant V but pressure increases

$\therefore$ Temperature increases, hence heating

Integer Type Questions

1. (7) : State functions are : enthalpy, entropy, pressure, volume, internal energy, temperature, free energy.

2. (5) : Density, temperature, pressure, viscosity, molar heat capacity.

3. (1) : $C_p = C_v + R$

$\therefore \quad C_p - C_v = 1\ R$

4. (4) : Heat supplied = Mass × Specific heat capacity × Rise in temperature.

$= m \times C_s \times \Delta T$

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$m = 1 \times 10^5 L = 1 \times 10^5 \times 10^3$.
$= 1 \times 10^8$ (density = 1 g cm^{-3})
$\Delta T = 25 - 15 = 10°C$
Heat supplied $= 1 \times 10^8 \times 4 \times 10$
$= 4 \times 10^9$ J or 4×10^6 kJ

5. (0) : For isothermal compression, $\Delta U = 0$

6. (4) : Given

$X \longrightarrow Y$; $\Delta_r G° = -193$ kJ mol^{-1}

$M^+ \longrightarrow M^{3+} + 2e^-$; $E° = -0.25$ V

Let 193 kJ energy is used for oxidising 'n' moles of M^+

For 1 mol of M^+,

$\Delta G° = -nFE°$
$= -2 \times 96500 \times (-0.25)$
$= 48250$ J mol or $= 48.250$ kJ

$\therefore$ Number of moles of M^+ oxidised when X is converted to Y

$$= \frac{193}{48.250} = 4$$

NCERT Exemplar Problems: MCQs Type I

1. (*c*):Thermodynamics is not concerned with rate at which a reaction proceeds.

2. (*c*): For a closed vessel made up of copper, no matter can exchange between the system and the surroundings but energy exchange can occur through its walls.

3. (*d*): $pV = nRT$
Thus, p, V, T and n (amount) describe the state of the system.

4. (*c*): The specific heat of a substance is the heat required to raise the temperature of 1 gram of a substance by one degree (1 K or 1° C). It is an intensive property and is independent of the volume of the substance.

6. (*b*): $\Delta_f H° = \Delta_f U° + \Delta n_g RT$
For the reaction,

$$C(s) + 2H_2(g) \longrightarrow CH_4(g)$$

$\therefore \quad \Delta n_g = 1 - 2 = -1$

$\therefore \quad \Delta_f H° = \Delta_f U° - 1RT$

or $\quad \Delta_f U° = \Delta_f H° + RT$

or $\quad \Delta_f H° < \Delta_f U°$

7. (*c*): Work done in free expansion of an ideal gas is zero.

$\therefore \quad w = 0$

Also, in an adiabatic process, $q = 0$

$\therefore \quad \Delta U = q + w = 0$

This means that during the process, ΔU remains constant. Therefore, during expansion no change in temperature takes place.

$\therefore \quad \Delta T = 0$

8. (*b*): w (reversible) < w (irreversible) because area under the curve in irreversible compression is more than the area under the curve for reversible compression.

9. (*c*): During the process of freezing, energy is released, which is absorbed by the surroundings.

$\therefore \quad \Delta S_{system} = -\frac{q_{rev}}{T}$;

$\Delta S_{surroundings} = \frac{q_{rev}}{T}$

Therefore, the entropy of the system decreases and that of surroundings increases.

10. (*c*):

$$C \text{ (graphite)} + O_2(g) \longrightarrow CO_2(g); \quad \Delta_r H = xkJ \text{ mol}^{-1} \quad ...(a)$$

$$C \text{ (graphite)} + \frac{1}{2}O_2(g) \longrightarrow CO(g); \quad \Delta_r H = ykJ \text{ mol}^{-1} \quad ...(b)$$

Subtracting equations (*a*) and (*b*) we get

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g); \quad \Delta_r H = zkJ \text{ mol}^{-1} \quad ...(c)$$

Equation (*c*) is obtained by subtracting (*a*) from (*b*) Therefore,

$$z = x - y$$

or $\quad x = y + z$

11. (*c*): The energy released in Eq. (*a*) is more than the energy released in Eq. (*b*) because in Eq. (*b*), some energy is used up to break the bonds of hydrogen molecule.

12. (*c*): The enthalpy of formation of a compound is the combination of elements to form a compound and it can be exothermic ($\Delta_f H° = -ve$) or endothermic ($\Delta_f H° = +ve$).

14. (*b*): ΔG cannot be +ve for a spontaneous reaction.

NCERT Exemplar Problems: MCQs Type II

16. (*a*, *b*) : In an exothermic reaction, heat is evolved by the system and hence q_p and ΔH are negative.

17. (*c*, *d*): (*a*) and (*b*) can neither occur by themselves nor by initiation. (*c*) can occur by itself. (*d*) can occur on initiation.

18. (*c*, *d*) : $w = -nRT \ln \frac{V_f}{V_i}$. Here, n, R and $\ln \frac{V_f}{V_i}$ are same in both the cases, therefore,

$$\frac{w_2}{w_1} = \frac{T_2}{T_1} \text{ or } \frac{w(600\,K)}{w(300\,K)} = \frac{600\ K}{300\ K} = 2$$

i.e. work done at 600K is twice the work done at 300K. Since each case involves isothermal expansion of an ideal gas, there is no change in internal energy *i.e.* $\Delta U = 0$.

19. (*a*, *c*): $\Delta H = H_p - H_r$. A negative value of ΔH shows that $H_r > H_p$ or $H_p < H_r$ *i.e.* Enthalpy of 2 moles of ZnO is less than enthalpy of 2 mol of zinc and one mol of oxygen by 693.8 kJ. Since $H_r > H_p$, 693.8 kJ of energy is evolved in the reaction.

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Unit Practice Test

for Board Examination

Time Allowed : 1 Hr. ***Maximum Marks : 25***

1. Neither q nor w is a state function but $q + w$ is a state function. Why? (1)

2. The enthalpy change for the reaction :

$$2NH_3\,(g) \longrightarrow N_2(g) + 3H_2(g)$$

is 92.2 kJ. What is the enthalpy of formation of NH_3? (1)

3. What is the basis of Hess's law of heat summation? (1)

4. What is the value of change of entropy at equilibrium? (1)

5. Write chemical equation for the enthalpy of combustion of ethanol. (1)

6. Explain :

(*i*) Reversible and irreversible process

(*ii*) Isothermal and adiabatic process. (2)

7. For the reaction at 300 K,

$$2\,A + B \longrightarrow C$$

$\Delta H = 450$ kJ mol^{-1} and $\Delta S = 0.2$ kJ K^{-1} mol^{-1}. At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range? (2)

8. Calculate the enthalpy of formation of ethane from the following enthalpy of combustion data :

C(s) : –393.5 kJ, H_2(g) : –285.8 kJ and C_2H_6(g) : –1560.0 kJ (2)

9. What is meant by entropy? Predict whether the following changes involve an increase or decrease of entropy :

(*i*) $Cr^{3+}\,(aq) + 6H_2O\,(g) \longrightarrow [Cr(H_2O)_6]^{3+}(aq)$

(*ii*) Sublimation of ammonium chloride.

(*iii*) Crystallization of salt from brine solution. (3)

10. At 60°C, dinitrogen tetroxide is 50% dissociated. Calculate standard free energy change at this temperature and at one atmosphere. (3)

11. A boy after swimming comes out from a pool covered with a film of water weighing 18 g. How much heat must be supplied to evaporate this water at 298 K ? Calculate the internal energy of vaporisation at 100°C. $\Delta H^\circ_{vap.}$ for water at 373 K = 40.66 kJ mol^{-1}. (3)

12. (*a*) Explain the following :

(*i*) Energy of the universe remains constant but entropy of universe always increases.

(*ii*) Most of the reactions which are spontaneous at room temperature are exothermic while the endothermic reactions are favoured only at very high temperature.

(*b*) Explain the state of chemical reactions when

(*i*) $\Delta G < 0$ (*ii*) $\Delta G > 0$ and (*iii*) $\Delta G = 0$

(*c*) Taking an example show that ΔS_{total} is the criterion for the spontaneity of a change. (2,2,1)

► To check your performance, see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part I of the book.

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UNIT 7

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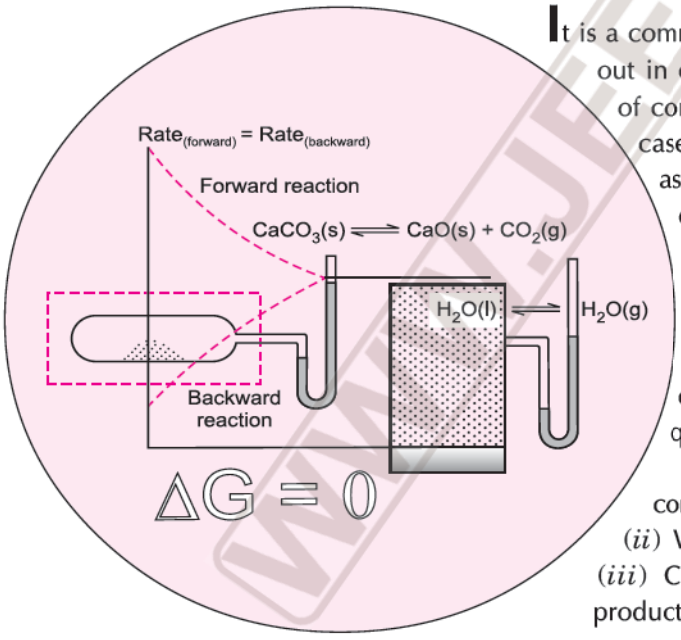

It is a common observation that most of the reactions when carried out in closed vessels do not go to completion under given set of conditions of temperature and pressure. In fact in all such cases, in the initial stage, only the reactants are present but as the reaction proceeds, the concentration of reactants decreases and that of products increases. Finally, a stage is reached when no further change in concentration of reactants and products is observed. At this state, there is a balance between reactants and products and the reaction appears to have stopped. This state is called **equilibrium state.** This raises the following curious questions in our mind:

(*i*) Why do reactions seem to stop before they reach to completion ?

(*ii*) What is the extent to which a reaction proceed ?

(*iii*) Can we modify the conditions to improve yield of products?

To know answers to these questions, we need to know about equilibrium and its nature.

Equilibrium can be established in both physical processes and chemical reactions.

PART A : PHYSICAL AND CHEMICAL EQUILIBRIUM

EQUILIBRIUM AND ITS DYNAMIC NATURE

Equilibrium *is* ***the state at which the concentrations of reactants and products do not change with time.***

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This state can be recognised by the constancy of certain measurable properties such as *pressure, density, colour, concentration*, etc. The amounts of reactants left depend on the experimental conditions such as concentration, temperature, pressure and the nature of the reaction. By changing these conditions of the system, we can control the extent to which a reaction proceeds. Now, a curious question comes to our mind. *What is the state of equilibrium?* To our eyes, it appears that nothing is happening at equilibrium. Though at macroscopic level, nothing appears to be happening, yet on a molecular level, there is a continuous change.

The important aspect of equilibrium system is the **reversibility.** Therefore, these are represented by double arrows indicating that the products coexist with reactants. For example, the equilibrium for the reaction of nitrogen and hydrogen to form ammonia may be represented as :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

In fact at equilibrium, both the forward and the backward reactions are still taking place. But the rates of forward and the backward reactions become equal. As a result, the concentration of each species becomes constant. The system is said to be in a **dynamic equilibrium.** Dynamic means **moving** and at a microscopic level, the system is in motion. Thus, although there is no apparent change at equilibrium yet both forward and backward reactions continue to take place and

Rate of forward reaction = Rate of backward reaction

The dynamic nature of equilibrium has also been discussed later in this chapter.

Though there are a large number and variety of chemical reactions, their state of chemical equilibrium may be classified into three groups depending upon the extent of the reaction.

(*i*) The chemical reactions which proceed nearly to completion and only negligible concentration of the reactants is left.

(*ii*) The chemical reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibrium stage.

(*iii*) The chemical reactions in which the concentrations of the reactants and the products are comparable at equilibrium.

The extent of a reaction in equilibrium depends upon the experimental conditions such as concentration of the reactants, temperature, pressure, etc. It is very important aspect for laboratory and industry to know the favourable conditions so that equilibrium is mostly in the direction of the desired product.

PHYSICAL AND CHEMICAL EQUILIBRIUM

The equilibrium may be classified as :

(*i*) Physical equilibrium. *The equilibrium set up in physical processes* is called **physical equilibrium**. For example, equilibrium in melting of ice to water, evaporation of water to steam, dissolution of sugar in water.

(*ii*) Chemical equilibrium. *The equilibrium set up in chemical processes* is called **chemical equilibrium.** For example, equilibrium in decomposition of calcium carbonate, reaction between hydrogen and iodine, etc.

Let us discuss nature of some common physical and chemical equilibrium systems.

EQUILIBRIUM IN PHYSICAL PROCESSES

We know that the substances exist in three states : *solid, liquid* and *gaseous*. The following three types of equilibria exist in these three states :

solid $\rightleftharpoons$ **liquid**

liquid $\rightleftharpoons$ **gas**

solid $\rightleftharpoons$ **gas**

In addition, there are equilibria involving dissolution of solids in liquids or gases in liquids.

Let us consider these equilibria briefly.

1. Solid-Liquid Equilibrium

Let us place some ice and water in a perfectly insulated thermos flask at 273 K and normal atmospheric pressure. Since the flask is insulated, there will be no exchange of heat between its contents and the surroundings. We notice that as long as the temperature remains constant, there is no change of mass of ice and water. *Does this mean that no change is taking place in this equilibrium*? If we could observe the individual molecules of ice and water, we would notice that a considerable activity is still taking place. Some molecules of liquid water are colliding against ice and are adhering on to the ice and at the same time, some molecules of ice go into the liquid. These two processes act in opposite directions to each other. Since there is no change in mass of ice and water, *the number of molecules going from water to ice are the same as the number of molecules going from ice to water*. In other words, the rate of transfer of molecules from ice into water (melting) and the rate of reverse transfer of molecules from water into ice (freezing) become equal. Therefore, the system shows constancy in concentration and is termed as *equilibrium state.* This state is represented as :

$$\underset{\text{ice}}{H_2O(s)} \rightleftharpoons \underset{\text{water}}{H_2O(l)}$$

At equilibrium : *Rate of melting = Rate of freezing*

The temperature at which the solid and the liquid phases are at equilibrium at atmospheric pressure is called the **normal freezing point** or **melting point** of that substance.

Thus at equilibrium, we can conclude that

- both the processes (melting and freezing) occur simultaneously.
- both the processes occur at the same rate so that the amount of the substance on both sides become constant.

2. Liquid-Vapour (or gas) Equilibrium

Let us consider the equilibrium between liquid water and its vapours during evaporation of water in a closed vessel.

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When liquid water is placed in a closed vessel at room temperature, it starts evaporating. As the process continues, more and more water molecules escape from liquid to the vapour state and pressure starts increasing. The change of pressure can easily be measured with the help of a manometer attached to the vessel as shown in Fig. 1. In the beginning, the mercury level in the two limbs of the manometer will be the same [Fig. 1 (*a*)]. As evaporation continues, the pressure goes on increasing and the level in the right hand limb starts rising.

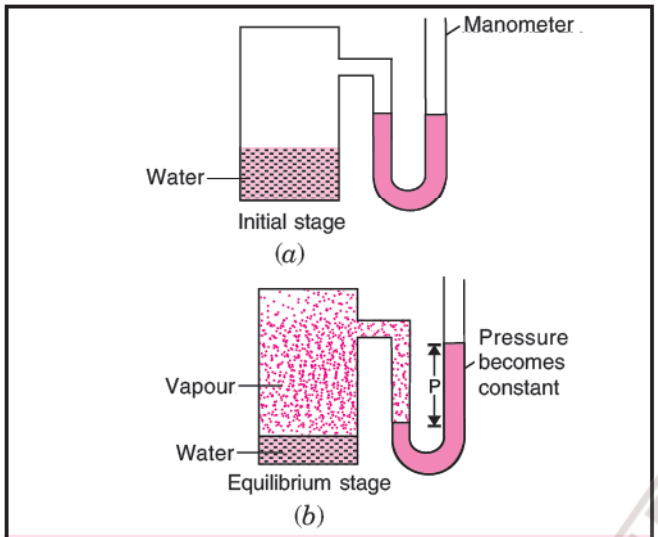

Fig. 1. Evaporation of water in a closed vessel.

After some time, it can be observed that pressure becomes constant indicating that no more water is evaporating even though some liquid water is still present [Fig. 1 (*b*)]. This represents an *equilibrium state* and may be represented as :

$$H_2O(l) \rightleftharpoons H_2O(g)$$

This process may be examined from **molecular point** of view. As evaporation progresses, the number of gaseous molecules in the vapour phase increases gradually. The molecules in the vapour phase move about at random in limited space and during their random movement, some of the molecules strike the surface of liquid and get condensed. This process of condensation acts in opposite direction to the process of vaporization. Initially, the rate of condensation is less than the rate of evaporation. But as evaporation proceeds, the concentration of molecules in vapour phase increases and therefore, the rate of condensation also increases. Finally, the number of molecules going into vapour phase become equal to the number of molecules returning to the liquid and therefore, the rate of evaporation becomes equal to the rate of condensation. At this stage, the system shows constancy in its pressure and is known as **equilibrium stage**. Thus, at equilibrium,

Rate of evaporation = Rate of condensation

The pressure exerted by the vapours in equilibrium with the liquid at a particular temperature is called **equilibrium vapour pressure** or **vapour pressure of the liquid** (refer Unit 5). This is constant at a particular temperature but varies with varying temperature. With the increase in temperature, the vapour pressure increases, however, it is independent of the amount of water in the vessel.

It may be noted that equilibrium cannot be attained if the process is carried out in an open vessel. This is obvious because in an open vessel, the reverse process *i.e.,* condensation of vapours back to water will not take place.

This process can be easily studied by a simple experiment as described below :

Take a small transparent box attached with a manometer as shown in Fig. 2. The box is first dried by placing some drying agent like anhydrous calcium chloride or phosphorus pentoxide for a few hours. Then the drying agent is removed by gently tilting the box on one side. Push a petri dish containing water quickly inside the box by tilting the box on one side [Fig. 2 (*a*)].

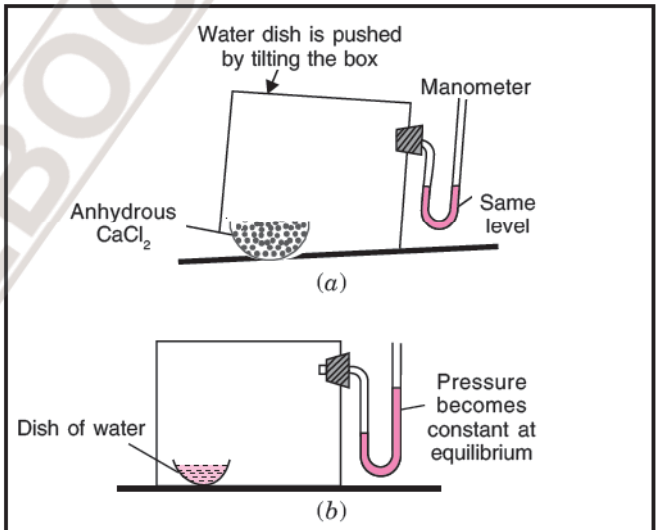

Fig. 2. An experiment for measuring the vapour pressure of water.

When we watch the manometer, we observe that the mercury levels in the limbs of the manometer were same in the beginning. But when petri dish is placed in the box, the mercury level in the right limb starts increasing and finally becomes constant. It may be noted that volume of water in petri dish has decreased. This state corresponds to equilibrium state and the pressure at this stage becomes equilibrium vapour pressure. If we repeat the experiment by taking different amounts of water in the petri dish, we observe that constant pressure recorded by the manometer comes out to be same as long as temperature remains constant.

When the above experiment is repeated with different liquids like methyl alcohol, ethyl alcohol and acetone, it would be observed that they have different

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vapour pressures at the same temperature. The liquid which has higher vapour pressure is more *volatile* and has lower boiling point. If we place three watch glasses containing separately 1 ml each of acetone, ethyl alcohol and water in the atmosphere and repeat the experiment with different volumes of the liquids in a warmer room, it is observed that in all such cases the liquid disappears eventually. The time taken for complete evaporation of the liquids depends upon the *(i) nature of the liquid, (ii) amount of the liquid and (iii) temperature.*

It may be noted that when the watch glass is open to the atmosphere, equilibrium is not achieved. This is because, the rate of evaporation remains constant but the molecules get dispersed into a large volume. As a result, there are very less chances for the molecules in the vapour phase to strike the surface of liquid and get condensed. Therefore, the rate of condensation is almost negligible. These are open systems and it *is not possible to attain equilibrium in an open system.*

Water and water vapour are in equilibrium position at atmospheric pressure (1 atm or 1.013 bar) and at 100°C in a closed vessel. The boiling point of water is 100°C at 1.013 bar pressure. For a liquid at atmospheric pressure (1.013 bar), the temperature at which the liquid and vapours are at equilibrium is called **boiling point** of the liquid. So, boiling point depends upon the atmospheric pressure. For example, boiling point of water depends on the altitude of the place. At high altitudes, the boiling point decreases because of decrease in atmospheric pressure (Unit 5).

3. Solid-Gas (or vapour) Equilibrium

Solid-gas equilibrium exists in systems where solids sublime to vapour. When we place some solid iodine in a closed vessel and warm it, iodine sublimes to iodine vapours. The vessel gets filled up with violet vapour and the intensity of colour increases with time. After sometime, the intensity of colour becomes constant. This state corresponds to equilibrium state. This may be represented as :

Rate of sublimation of solid I_2 to form vapour =
Rate of condensation of I_2 vapour to solid

This may be represented as:

$$I_2\,(\text{solid}) \rightleftharpoons I_2\,(\text{vapour})$$

Some other examples showing this type of equilibrium are :

$$NH_4Cl\,(\text{solid}) \rightleftharpoons NH_4Cl(\text{vapour})$$
$$\text{Camphor}\,(\text{solid}) \rightleftharpoons \text{Camphor}\,(\text{vapour})$$

Equilibrium involving Dissolution of Solids in Liquids and Gases in Liquids

(i) Solids in liquids

When we add a small quantity of sugar to about 100 *m*L of water at 273 K, sugar dissolves. If we add more sugar to this solution, it also dissolves. Such a solution is said to be **unsaturated.** However, if we continue adding sugar to the same amount of water at the same temperature, a stage is reached when no more sugar appears to dissolve. (Fig. 3).

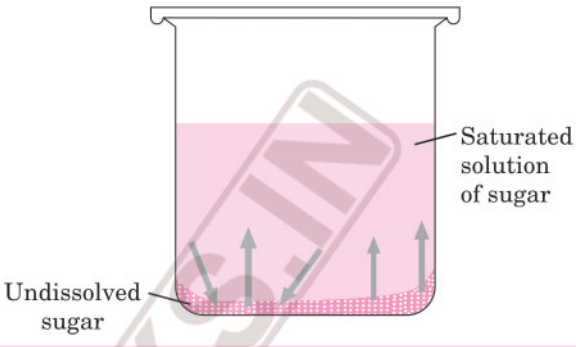

Fig. 3. Equilibrium between dissolved sugar and undissolved sugar in a saturated solution.

At this point, the solution is said to be **saturated.** Once the solution becomes saturated, then the concentration of sugar in the solution becomes constant. This indicates that a *state of equilibrium has been reached between the undissolved sugar and dissolved sugar.*

This may be represented as :

$$\text{Sugar (in solution)} \rightleftharpoons \text{Sugar (solid)}$$

At this stage, the number of molecules of sugar going into the solution (*dissolution process*) becomes equal to the number of sugar molecules depositing back on the undissolved sugar from the solution (*crystallisation process*). Therefore, at equilibrium, the rate of dissolution of sugar becomes equal to rate of crystallisation of sugar. Thus at equilibrium,

Rate of dissolution of sugar =
Rate of crystallisation of sugar

(ii) Gases in liquids

Gases can be dissolved in suitable liquids. At a given temperature, a liquid can dissolve only a certain definite mass of the gas. This suggests that a state of equilibrium exists between the molecules in the gaseous state and the molecules dissolved in the liquid. For example, when carbon dioxide is dissolved in soda water, the following equilibrium exists :

$$CO_2(g) \rightleftharpoons CO_2\ (\text{in solution})$$

The solubility of a gas in the liquid depends on the pressure. The dependence of the solubility of a gas and its pressure above the solvent is given by a law known as **Henry's law.** According to **Henry's law,**

the mass of a gas dissolved in a given mass of a solvent at a particular temperature is proportional to the pressure of the gas above the solvent.

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$$m \propto p$$

or $$m = kp$$

As discussed above, in soda water bottles, the gaseous carbon dioxide exists in equilibrium with the carbon dioxide dissolved in water. When the soda water bottle is opened, the carbon dioxide dissolved in it escapes out rapidly with fizz. The fizzing out of soda bottle can be easily understood in terms of **Henry's law.**

The soda bottles are sealed by adding carbon dioxide gas at high pressures (above atmospheric pressure). Because of high pressure, there is plenty of gas dissolved in water. When the soda bottle is opened, the pressure of the gas inside the bottle is considerably decreased (atmospheric pressure). Since the solubility of the gas is proportional to the pressure, the solubility decreases considerably. As a result, the gas escapes from the solution rapidly with fizz. However, if the soda bottle is left open to air for some time, it does not fizz any more because the pressure inside the bottle and outside is the same *i.e.,* atmospheric pressure.

The solubility of a gas in a liquid decreases with increase in temperature.

Sum up

From the physical equilibria studied above, we have noticed that at equilibrium, some measurable properties of the system become constant. For example,

(*i*) In case of liquid $\rightleftharpoons$ gas equilibrium, *the pressure of the vapour* above the liquid becomes constant at a particular temperature. *e.g.,*

$$H_2O(l) \rightleftharpoons H_2O(g)$$

pH_2O is constant.

(*ii*) For solid $\rightleftharpoons$ liquid equilibrium, the two phases can co-exist only at a *definite temperature* (called melting point or freezing point) at 1 atm (1.013 bar) pressure, *e.g.,*

$$H_2O(s) \rightleftharpoons H_2O(l)$$

temperature (melting point) is constant.

(*iii*) For dissolution of solid in liquid; solid $\rightleftharpoons$ solution, the *solubility is constant at a given temperature. e.g.,*

$$\text{Sugar (undissolved)} \rightleftharpoons \text{Sugar } (aq)$$

solubility is constant.

(*iv*) For dissolution of gases in liquids, *the concentration of a gas in liquid* at a given temperature is proportional to the pressure of the gas over the liquid, *e.g.,*

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

$$[CO_2(aq)] \propto p_{CO_2} \quad \text{or} \quad [CO_2(g)]$$

or $$\frac{[CO_2(aq)]}{[CO_2(g)]} \text{ is constant.}$$

These are summarised in Table 1.

General Characteristics of Physical Equilibria

The **general characteristics** of equilibria involving physical processes are summed up as :

1. The measurable properties of the system become constant at equilibrium.

2. Equilibrium can be established only in case of closed system i.e., the system should neither gain matter from the surroundings nor lose matter to the surroundings.

3. At equilibrium, both the opposing processes occur at the same rate i.e., equilibrium is dynamic.

Table 1. Expressions which acquire constant value at equilibrium.

Process	Expression, which acquires constant value at equilibrium.
Liquid $\rightleftharpoons$ Vapour *e.g.,* $H_2O(l) \rightleftharpoons H_2O(g)$	pH_2O at constant temperature.
Solid $\rightleftharpoons$ Liquid *e.g.,* $H_2O(s) \rightleftharpoons H_2O(l)$	Melting point at constant pressure.
Solute $(s) \rightleftharpoons$ Solute (solution) *e.g.,* Sugar $(s) \rightleftharpoons$ Sugar (in solution)	Concentration of the solute in solution is constant at a given temperature. Concentration of sugar (solution) at constant temperature.
Gas $(g) \rightleftharpoons$ Gas (aq) *e.g.,* $CO_2(g) \rightleftharpoons CO_2(aq)$	[Gas (aq)/gas(g)] is constant at a given temperature. Ratio of concentration of $CO_2(aq)$ and $CO_2(g)$ *i.e.,* $[CO_2(aq)]/[CO_2(g)]$ at constant temperature.

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4. When equilibrium is attained, there exists an expression of concentrations of the substances involved in equilibrium which becomes constant at a given temperature.

5. The magnitude of the constant value of the concentration related expression (called equilibrium constant) gives an indication of the extent to which the reaction proceeds before acquiring equilibrium.

Experiment to illustrate dynamic nature of physical equilibrium

Consider a saturated solution of sugar in a beaker. As we know that in the saturated solution, no more sugar can dissolve as long as we keep the temperature constant. Thus, there exists an equilibrium between the sugar dissolved in solution and sugar which remains undissolved.

Let us add some radioactive sugar into this saturated solution of non-radioactive sugar (Fig. 4). When we analyse the sugar solution, we observe that the solution contains some radioactive sugar. Now, if no dissolution is occurring at equilibrium, we should not get any radioactive sugar in solution. However, the presence of radioactive sugar in solution indicates that some radioactive sugar has passed from undissolved sugar to exchange some non-radioactive sugar in the solution.

This experiment shows that even at equilibrium, the processes of dissolution and precipitation are occurring and therefore, the equilibrium is dynamic in nature. *However at equilibrium,

Rate of dissolution = Rate of precipitation

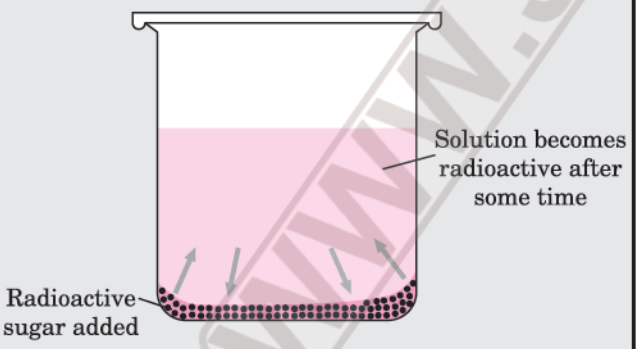


Fig. 4. Demonstration of dynamic nature of solid in liquid equilibrium.

SOLVED EXAMPLES

Example 1.

The solubility of iodine in water is 1.1×10^{-3} mol L^{-1} at 288 K. When 0.200 g of iodine is stirred in 100 of water till equilibrium is reached, what will be the mass of iodine found in solution and the mass that is left undissolved. After equilibrium is reached with 0.200 g of iodine and 100 of water, we add 150 of water to the system. How much iodine will be dissolved and how much will be left undissolved and what will be the concentration of iodine in solution ? ***N.C.E.R.T.***

Solution: Solubility of iodine = 1.1×10^{-3} mol L^{-1}

This means that 1.1×10^{-3} mol of iodine is present in 1 L of water.

Molar mass of iodine = 254

$\therefore$ Amount of iodine dissolved per litre of water $= 1.1 \times 10^{-3} \times 254 =$ **0.279 g**

The amount of iodine dissolved per 100 of water

$$= \frac{0.279}{1000} \times 100 = \textbf{0.0279 g}$$

Amount of iodine added = 0.200 g

$\therefore$ Amount of undissolved iodine in 100 mL of water $= 0.2 - 0.0279 =$ **0.172 g**

When 150 cm^3 of water is added after the equilibrium, the total volume becomes 100 + 150 = 250 cm^3

$$\text{Now iodine dissolved in 250 of water} = \frac{0.279 \times 250}{1000} = \textbf{0.07 g}$$

Amount of undissolved iodine = 0.2 – 0.07 = **0.13 g**

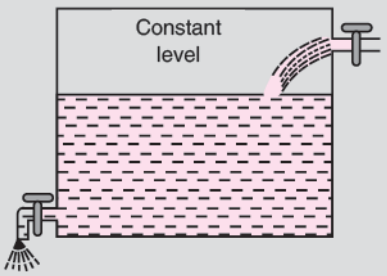
Molar concentration of iodine

$$= \frac{0.07g}{254g\ mol^{-1} \times 250} \times \left(\frac{1000}{1L}\right) = 0.0011\ mol\ L^{-1}$$

EQUILIBRIA INVOLVING CHEMICAL SYSTEMS

There are many chemical reactions in which the products formed during the reaction, react to give back the original reactants. These types of reactions are called reversible reactions. Thus, ***reversible reactions** are **the reactions in which the products formed can also react with one another under suitable conditions to give back the reactants.*** In other words, in reversible reactions, the reactions take place in both the forward and backward directions.

* The dynamic state of equilibrium can be compared to water tank having an inlet and outlet. Water in the tank can remain at the same level if the rate of flow of water from inlet (compared to rate of forward reaction) is made equal to the rate of flow of water from outlet (compared to rate of backward reaction). Thus, the water level in the tank remains constant, though both the inlet and outlet of water are working all the time.



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For example, the reaction between gaseous hydrogen and iodine vapours to give gaseous hydrogen iodide is a reversible reaction and may be expressed as :

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Similarly, some other reversible reactions are :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

On the other hand, ***the chemical reactions in which the products formed do not combine to give back the reactants*** are known as ***irreversible reactions.*** For example, potassium chlorate decomposes on heating to form potassium chloride and oxygen :

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

In this reaction, the products cannot combine to give back potassium chlorate. In the case of irreversible reactions, the reactions occur only in the forward direction. These reactions go to completion and no starting materials are left. However, the reversible reactions do not go to completion. When these reactions are performed in closed containers, a stage is reached at which the reactions appear to stop even though some starting materials are left. This state is called **chemical equilibrium.** As in physical equilibria, this state may be recognised by the constancy of some measurable properties.

Let us consider a few chemical reactions in order to understand chemical equilibrium.

1. Decomposition of calcium carbonate

When solid calcium carbonate is heated in a closed vessel at 1073 K, it decomposes into solid calcium oxide and gaseous carbon dioxide. Due to the production of CO_2, pressure will be developed in the vessel, which can be recorded with the help of a manometer (Fig. 5).

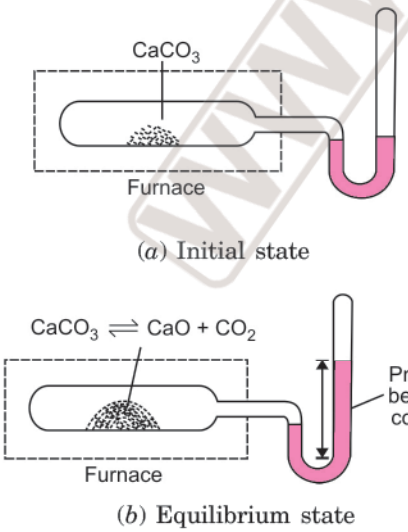

Fig. 5. Decomposition of calcium carbonate at 1073 K.

As the decomposition of calcium carbonate continues, the pressure goes on increasing. After some time, it is observed that pressure becomes constant at constant temperature even though some $CaCO_3$ is still present. This means that the amount of CO_2 produced has become constant.

This constancy of pressure tells us that the equilibrium has been reached. This may be represented as :

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

2. Combination of hydrogen and iodine

When hydrogen gas and iodine vapours are heated in a closed vessel at a constant temperature, 717 K, the two react to form hydrogen iodide (Fig. 6). In the beginning, the colour of the reaction mixture is deep violet due to the presence of iodine. But as the reaction proceeds, the intensity of the colour decreases as more and more iodine reacts with hydrogen to form hydrogen

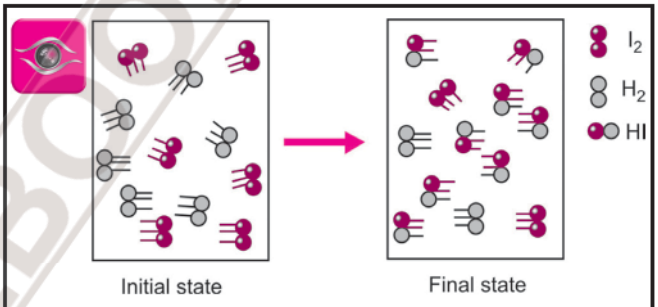

Fig. 6. Reaction between H_2 and I_2 to form HI.

iodide. After some time, the intensity of the colour of the reaction mixture becomes constant even though some reactants are still present. *This constancy of intensity of colour* indicates that the concentrations of both the reactants and products have become constant and *state of equilibrium has been attained.*

There are many other examples which can be cited to support the fact that most of the reactions or processes *appear to stop* after some time although, the forward and backward reactions are occurring. Thus, the equilibrium may be summed up as

> ***the state in which the measurable properties of the system (such as pressure, density, colour or concentration) do not undergo any further noticeable change under given set of conditions*** *is said to be a* **state of equilibrium.**

Attainment of Equilibrium

To understand the meaning of chemical equilibrium, consider a simple general reversible reaction carried in a closed vessel at a constant temperature.

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

At the start of the experiment, the reactants A and B are present in definite concentrations. As the reaction proceeds, the effective collisions among the

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reactant molecules result in the formation of the products.

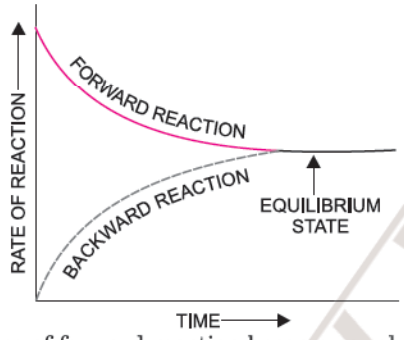
The forward reaction may be written as :

$$A + B \longrightarrow C + D \quad \text{Forward reaction}$$

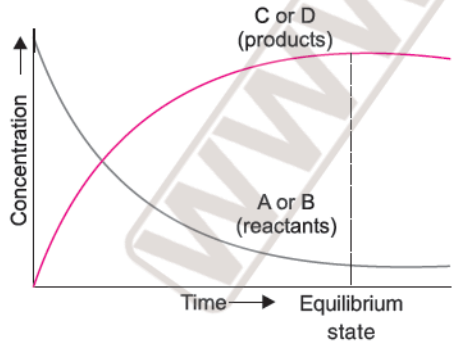
With the passage of time, the concentration of the reactants decreases while those of the products increases. Since the product molecules are not allowed to leave the vessel (reaction is carried out in the closed container), they also react back among themselves to give back the reactants. The backward reaction may be written as :

$$C + D \longrightarrow A + B \quad \text{Backward reaction}$$

This means that the chemical reaction proceeds in both ways and is called a *reversible reaction*. As the reaction progresses, the concentration of the reactants decreases and therefore, the rate of the forward reaction falls off with time. On the other hand, the rate of backward reaction increases because of the increase in concentration of the products. The two rates approach each other and finally a state is achieved at which the two rates become equal and the concentrations of products (C or D) and reactants (A or B) become constant. This state is called *equilibrium state*. This has been shown in Fig. 7.



(*a*) Rates of forward reaction become equal to rate of backward reaction.



(*b*) Concentrations of reactants and products become constant.

Fig. 7. Attainment of equilibrium in a reversible reaction.

The same state of equilibrium is reached if we start with C and D when no A and B are present initially. Even after the equilibrium is achieved, forward and backward reactions continue to occur at equal rates and do not stop. Thus, the equilibrium can be attained from either direction.

Thus, at **equilibrium,**

Rate of forward reaction = Rate of backward reaction

Characteristics of Chemical Equilibrium

The chemical equilibrium has the following characteristics :

1. Chemical equilibrium is dynamic in nature. The constancy of observable properties in an equilibrium system does not mean that the reaction has stopped altogether. It may be noted that after the attainment of equilibrium the reaction does not stop though it appears as if it has stopped. In fact, both the forward and backward reactions continue even after attaining the equilibrium. But the rates of two opposing reactions become equal. This means that if some products are formed from the reactants, exactly equivalent amount of products are going back to the reactants. For example, if during the reaction between H_2 and I_2 to form HI, certain amount of hydrogen iodide is formed by the combination of hydrogen and iodine, then exactly same amount of hydrogen iodide gets decomposed to give back H_2 and I_2.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

This is so because the rate of formation of HI at the equilibrium becomes equal to the rate of decomposition of HI. As a result of this, the concentrations of reactants and products become constant. Since both the opposing reactions continue (at the same rate), even after the equilibrium has been reached, such a chemical equilibrium is known as **dynamic equilibrium.**

Demonstration of dynamic nature of chemical equilibrium

The dynamic nature of chemical equilibrium can be demonstrated by taking the example of synthesis of ammonia by the Haber's process. Haber performed a series of experiments, starting with known amounts of nitrogen and hydrogen maintained at high temperature and pressure. He determined the amount of ammonia present and concentration of hydrogen and nitrogen at different intervals of time. He plotted the graph of concentration of H_2, N_2 (unreacted) and NH_3 (formed) at different time intervals as shown in Fig. 8. The figure shows that after a certain time, the composition of the mixture becomes same even though some of the reactants are still present. *This constancy in composition indicates that the reaction has reached equilibrium stage.*

In order to understand the dynamic nature of equilibrium, the experiment was carried out with exactly the same conditions of temperature and pressure but using D_2 (deuterium, an isotope of

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hydrogen) in place of H_2. It was observed that the reaction mixtures starting with either H_2 or D_2 reached the equilibrium with the same composition except that ND_3 and D_2 were present instead of NH_3 and H_2. After the equilibrium is attained, these two reaction mixtures (H_2, N_2, NH_3 and D_2, N_2 and ND_3), are mixed together and left for some time. When later this mixture is analyzed, it was observed that the concentration of NH_3 is just the same as before. However, when this mixture is analyzed by mass spectrometer, it is observed that all deuterium containing forms of ammonia (NH_3, NH_2D, NHD_2 and ND_3) and hydrogen (H_2, HD and D_2) are present in the mixture. What does this mean ? Now, if the reaction had stopped at equilibrium stage, then there would have been no mixing of isotopes and we would not have found NH_2D, NHD_2 or HD in the reaction mixture. Thus, we can conclude that the mixing of H and D atoms in the molecules must be due to the continuation of the forward and the backward reactions in the mixture. In other words, the equilibrium is dynamic in nature.

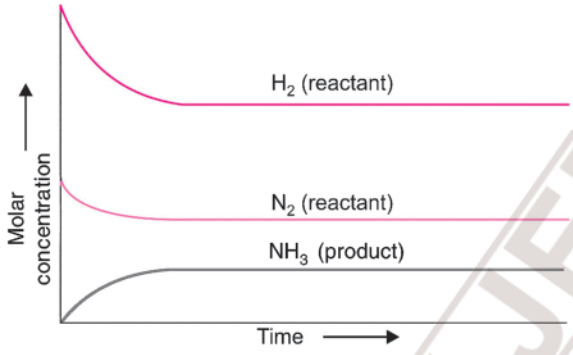

Fig. 8. Equilibrium for the reaction :
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

2. The properties of the system become constant at equilibrium and remain unchanged thereafter. For example, in the decomposition of $CaCO_3$ and evaporation of water in closed vessel, pressure becomes constant at equilibrium.

3. The equilibrium can be attained only if the system is closed one. For the establishment of equilibrium, it is quite obvious that the system should be closed one. If the system is not closed, some of the products may escape from the container and therefore, the backward reaction will not take place. Consequently, it will not be possible to attain the equilibrium.

4. The equilibrium can be approached from either direction. Equilibrium can be attained from both sides whether we start the reaction by taking H_2 (g) and I_2 (g) and get HI (g) or by taking HI (g) which will decompose to H_2 (g) and I_2 (g).

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Let us consider this reaction. If we start with equal initial concentration of H_2 and I_2, the reaction proceeds in the forward direction and the concentration of H_2 and I_2 decreases and that of HI increases. After some time, the concentration of all these three (H_2, I_2 and HI) become constant when the equilibrium is reached. We can also start the reaction by decomposing HI and the reaction proceeds in the reverse direction. It is observed that the concentration of HI decreases and that of H_2 and I_2 increases until they all become constant and equilibrium is reached. These results are shown in Fig. 9. It is observed that if the total number of H and I atoms are same in a given volume, the same equilibrium mixture is obtained whether we start it from pure reactants (H_2 and I_2) or products (HI).

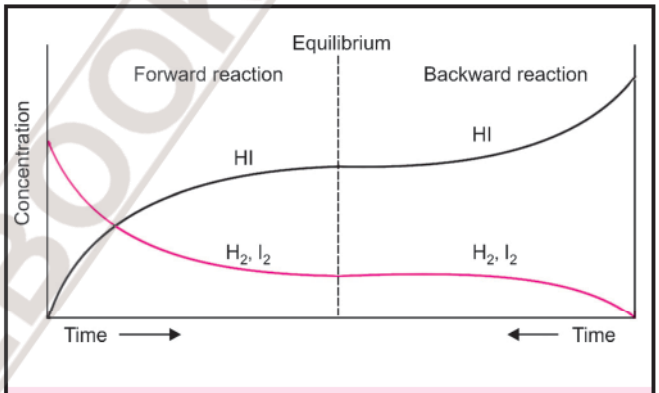

Fig. 9. Chemical equilibrium in the reaction :
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, attained from either direction.

This can be proved with the help of a very simple experiment of equilibrium between nitrogen tetraoxide N_2O_4 (colourless gas) and nitrogen dioxide, NO_2 (a reddish brown gas).

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
Colourless (at 273 K) — Reddish brown (at 373 K)

It is observed that at ordinary temperature, say 298 K, the two gases exist as equilibrium mixture having pale brown colour. At very low temperature (273 K), N_2O_4 is stable and exists as pure N_2O_4 (colourless gas). When temperature is increased, it decomposes to NO_2. At 373 K, it decomposes almost completely to NO_2 which is dark brown in colour.

Take two identical flasks A and B. Fill them with nitrogen dioxide and seal them. Place the flask A in an ice bath and the flask B in boiling water as shown in Fig. 10.

The gas in flask A (placed in ice bath) becomes almost colourless and consists of mostly N_2O_4 molecules. On the other hand, the gas in flask B (placed in boiling water) has reddish brown colour and consists of mainly NO_2 molecules.

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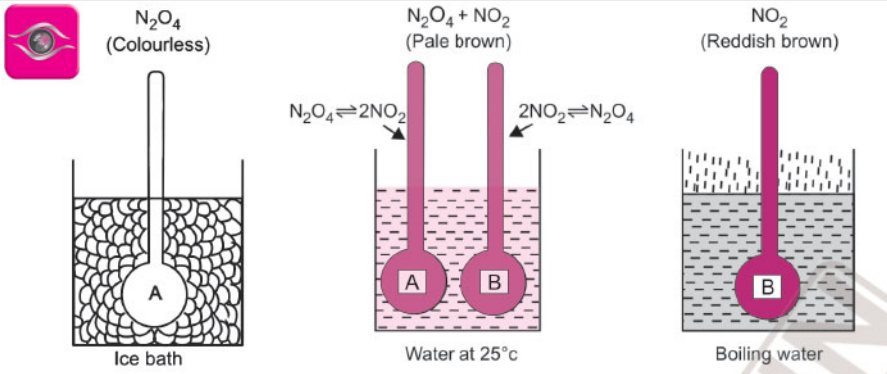

Fig. 10. Demonstration of equilibrium between N_2O_4 and NO_2.

Now transfer both the flasks into a bath maintained at 298 K and observe the change in colour. The colour of the gas in flask A starts changing into brown colour indicating, thereby, the gradual conversion of N_2O_4 into NO_2.

$$\underset{\text{Colourless}}{N_2O_4(g)} \longrightarrow \underset{\text{Reddish brown}}{2NO_2(g)} \qquad \text{(Flask A)}$$

During the same interval, the reddish brown colour in flask B begins to fade and becomes pale brown indicating the gradual change of NO_2 to N_2O_4. This may be represented as :

$$\underset{\text{Reddish brown}}{2NO_2(g)} \longrightarrow \underset{\text{Colourless}}{N_2O_4(g)} \qquad \text{(Flask B)}$$

After some time, when both the flasks attain the temperature of the bath, the colour in two flasks become identical and no further change in colour occurs. This constancy of colour indicates that equilibrium has been attained in both cases and both contain mixture of NO_2 and N_2O_4 of the same composition. The experiment clearly demonstrates that the equilibrium can be approached from either direction.

5. A catalyst does not alter the equilibrium point. In a reversible reaction, a catalyst increases the rate of forward as well as backward reaction to the equal extent. Therefore, the equilibrium point is not altered. However, the equilibrium may be attained earlier in the presence of a catalyst.

LAW OF MASS ACTION

On the basis of observations of many equilibrium reactions, two Norwegian chemists Cato Maximillian Guldberg and Peter Waage suggested (1864) a quantitative relationship between the rates of reactions and the concentration of the reacting substances. This relationship is known as **law of mass action.** It states that

the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants at a constant temperature at any given time.

The molar concentration *i.e., number of moles per litre* is also called ***active mass.*** It is expressed by enclosing the symbols of formulae of the substance in square brackets. For example, molar concentration of A is expressed as [A].

Let us consider a simple reaction between the species A and B :

$$A + B \longrightarrow \text{Products}$$

According to law of mass action,

$$\text{Rate of reaction, } r \propto [A][B] = k[A][B]$$

where [A] and [B] are the molar concentrations of the reactants A and B respectively, k is a constant of proportionality for the forward reaction and is known as **rate constant.** The rate constant is also called **velocity constant.** Now, if the concentration of each of the reactants involved in the reaction is unity *i.e.,* [A] = [B] = 1, then

$$\text{Rate of reaction, } r = k \times 1 \times 1 \text{ or } r = k$$

Thus, the rate constant of a reaction at a given temperature may be defined as *the rate of the reaction when the concentration of each of the reactants is unity.*

Consider the reaction,

$$2A + 3B \longrightarrow \text{Products}$$

According to the law of mass action,

Rate at which A reacts $\propto$ [A] [A] or $[A]^2$

Rate at which B reacts $\propto$ [B] [B] [B] or $[B]^3$

$\therefore$ Rate of reaction between A and B $\propto [A]^2 [B]^3$

or Rate of reaction $= k[A]^2[B]^3$

For a general reaction,

$$aA + bB + cC \longrightarrow \text{Products}$$

The law of mass action may be written as :

$$\text{Rate of reaction, } r = k\ [A]^a [B]^b [C]^c$$

Thus, the **law of mass action may** be re-stated as :

the rate of a chemical reaction at any particular temperature is proportional to the product of the molar concentrations of reactants with each concentration term raised to the power equal to the number of molecules of the respective reactants taking part in the reaction.

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The number of molecules of a reactant taking part in a reaction is also called its **stoichiometric coefficient.** For example, *a, b* and *c* .... in the above equation are called **stoichiometric coefficients** of A, B and C .... respectively.

LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

The law of mass action may be applied to a reversible reaction to derive a mathematical expression for equilibrium constant known as **law of chemical equilibrium.**

Let us consider a simple reversible reaction,

$$A + B \rightleftharpoons C + D$$

in which an equilibrium exists between the reactants (A and B) and the products (C and D). The forward reaction is

$$A + B \longrightarrow C + D$$

According to law of mass action,

$$\textit{Rate of forward reaction} \propto [A][B] = k_f [A][B]$$

where k_f is the rate constant for the forward reaction and [A] and [B] are molar concentrations of reactants A and B respectively.

Similarly, the backward reaction is :

$$C + D \longrightarrow A + B$$

$$\textit{Rate of backward reaction} \propto [C][D] = k_b[C][D]$$

where k_b is the rate constant for the backward reaction and [C] and [D] are molar concentrations of products C and D respectively.

At equilibrium, the rates of two opposing reactions become equal. Therefore, at equilibrium,

Rate of forward reaction = Rate of backward reaction

$$k_f[A][B] = k_b[C][D]$$

or
$$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

or
$$K = \frac{[C][D]}{[A][B]}$$

The combined constant, K, which is equal to k_f/k_b is called **equilibrium constant** and has a constant value for a reaction at a given temperature. The above equation is known as **law of chemical equilibrium.**

The concentration ratio *i.e.,* ratio of the product of concentrations of products to that of reactants is also known as **concentration quotient** and is denoted by **Q.**

$$\text{Concentration quotient, } Q = \frac{[C][D]}{[A][B]}$$

It may be noted that Q becomes equal to equilibrium constant (K) when the reaction is at the equilibrium state.

Thus at equilibrium,

$$Q = K$$

For a general reaction of the type :

$$aA + bB \rightleftharpoons cC + dD$$

The equilibrium constant may be represented as :

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where the exponents *a, b, c* and *d* have the same values as those in the balanced chemical equation. Thus, **the equilibrium constant** may be defined as :

the ratio between the product of molar concentrations of the products to that of the molar concentrations of the reactants with each concentration term raised to a power equal to its stoichiometric coefficient in the balanced chemical equation at a constant temperature.

For example, for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

the equilibrium constant, K_c may be written as

$$K_c = \frac{[HI(g)]^2_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$$

Generally, the subscript 'eq' (used for expressing equilibrium concentrations) is omitted. It is taken for granted that the concentrations in the expression for K_c are equilibrium values. Therefore, we may write,

$$K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

In the above expression, the concentrations of the various species are generally expressed in terms of moles/litre. The molar concentrations of different species are indicated by enclosing these in square brackets. The equilibrium constant may be written as K_c, where the subscript *'c'* indicates that the equilibrium constant is expressed in terms of molar concentrations.

It may be noted that after the equilibrium is established the value of K_c is constant at a given temperature irrespective of the initial concentrations of $H_2(g)$, $I_2(g)$ and $HI(g)$ taken in the closed vessel.

Similarly, the equilibrium constant for the reaction :

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$$

$$K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$$

It may be noted that while writing expression for equilibrium constant, symbols for phases (*s, l, g*) are ignored unless it is very essential.

Equilibrium Constant in Gaseous Systems

In gaseous reactions, *the concentration of gases*

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may also be expressed in terms of their partial pressures. For a gaseous reaction,

$$aA + bB \rightleftharpoons cC + dD$$

The equilibrium constant may be represented as:

$$K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b}$$

where p_A, p_B, p_C and p_D are the partial pressures of the gases A, B, C and D respectively. K_p is not always equal to K_c (equilibrium constant defined in terms of concentrations).

Relationship between K_p and K_c.

For the reaction,

$$aA + bB \rightleftharpoons cC + dD$$

the equilibrium constant for the reaction expressed in terms of the concentrations (mol/litre) may be expressed as :

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad ...(i)$$

If the equilibrium involves gaseous species, then the concentrations may be expressed in terms of partial pressures of the gaseous substances. The equilibrium constant in terms of partial pressures may be written as :

$$K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} \quad ...(ii)$$

where p_A, p_B, p_C and p_D represent partial pressures of the substance A, B, C and D respectively. If gases are assumed to be ideal, then according to ideal gas equation,

$$pV = nRT$$

or $$p = \frac{n}{V} RT$$

where p is the pressure in Pa, n is the amount of the gas in mol, V is the volume in m^3 and T is the temperature in Kelvin.

$$\frac{n}{V} = \text{concentration, C}$$

We can also write

$$p = CRT \text{ or } [\text{gas}]\, RT \quad ...(iii)$$

If C is in mol dm^{-3} and p is in bar, then R = 0.0831 bar dm^3 mol^{-1} K^{-1}. Therefore, at constant temperature, pressure of the gas is proportional to its concentration, *i.e.*

$$p \propto C$$

or $$p \propto [\text{gas}]$$

Now $p = CRT$ so that

$$p_A = [A]RT$$

where [A] is the molar concentration of A. Similarly,

$$p_B = [B]\, RT$$

$$p_C = [C]\, RT$$

$$p_D = [D]\, RT$$

where [B], [C] and [D] are the molar concentrations of B, C and D respectively.

Substituting these values in expression for K_p (eq. *ii*)

$$K_p = \frac{([C]RT)^c \cdot ([D]RT)^d}{([A]RT)^a \cdot ([B]RT)^b}$$

$$= \frac{[C]^c [D]^d (RT)^{c+d}}{[A]^a [B]^b (RT)^{a+b}}$$

$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d)-(a+b)}$$

$$= K_c (RT)^{(c+d)-(a+b)}$$

$$= K_c (RT)^{\Delta n_g}$$

where $\Delta n_g = (c + d) - (a + b)$

i.e., number of moles of gaseous products – number of moles of gaseous reactants in the balanced chemical equation.

Thus, $\boxed{K_p = K_c (RT)^{\Delta n_g}}$

For example,

(*i*) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_p = K_c (RT)^{\Delta n_g}$$

$$\Delta n_g = 2 - (1 + 3) = -2$$

$$\therefore \quad K_p = K_c (RT)^{-2}$$

(*ii*) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$\Delta n_g = 2 - (1 + 1) = 0$$

$$\therefore \quad K_p = K_c (RT)^0 = K_c$$

(*iii*) $2\,NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

$$\Delta n_g = 2 + 1 - 2 = 1$$

$$\therefore \quad K_p = K_c (RT)^1 = K_c RT$$

It may be noted that while calculating the values of K_c from K_p or vice versa, **the units of R must be used carefully.**

* If the partial pressures are taken in atmospheres, the value of R should be used as 0.0821 litre atm K^{-1} mol^{-1}.
* If the partial pressures are expressed in bars, the value of R should be used as 0.0831 litre bar K^{-1} mol^{-1}.

Temperature (T) will always be used in degree Kelvin (K). We have seen in Unit 1

1 pascal, Pa = 1 Nm^{-2} and 1 bar = 10^5 Pa

K_p values of some common reactions at different temperatures are given in Table 2.

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Table 2. Equilibrium constant, K_p for some common reactions.

Reaction	Temperature (K)	K_p
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	298	6.8×10^5
	400	41
	500	3.6×10^{-2}
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	298	0.98
	400	47.9
	500	1700
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	298	4.0×10^{24}
	500	8.5×10^{10}
	700	3.0×10^4
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	298	795
	500	160
	700	54

It is clear from the above table that the equilibrium constant changes appreciably with temperature.

Units of Equilibrium Constant

The equilibrium constant expression involves the concentrations or partial pressures of the reactants and the products. The units of K will depend upon the number of moles of reactants and products involved in the reaction as discussed below :

(*i*) *When total number of moles of products is equal to the total number of moles of reactants, K* **has no units.** For example, consider the reaction,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

$$K = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]}$$

If the concentrations are expressed in terms of moles per litre, then

$$\frac{(\text{mol L}^{-1})^2}{(\text{mol L}^{-1})(\text{mol L}^{-1})} = \textbf{no units}$$

Similarly, for the reaction

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

$$K = \frac{[H_2(g)][I_2(g)](\text{mol L}^{-1})(\text{mol L}^{-1})}{[HI(g)]^2 (\text{mol L}^{-1})^2}$$

$$= \textbf{no units}$$

(*ii*) *When total number of moles of products is different than the total number of moles of reactants.* In such a reaction *K* has units. For example, consider the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$

The units of K are

$$= \frac{(\text{mol L}^{-1})^2}{(\text{mol L}^{-1})(\text{mol L}^{-1})^3}$$

$$= \textbf{L}^2\ \textbf{mol}^{-2}$$

Similarly, the units of the reaction :

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$$

$$K = \frac{[FeSCN^{2+}(aq)]}{[Fe^{3+}(aq)][SCN^-(aq)]}$$

$$\text{Units} = \frac{(\text{mol L}^{-1})}{(\text{mol L}^{-1})(\text{mol L}^{-1})} = \textbf{L mol}^{-1}$$

Thus, it may be concluded that equilibrium constant K has no units *i.e.*, dimensionless if the total number of moles of the products is exactly equal to the total number of moles of reactants. On the other hand, if the number of moles of products and reactants are not equal, K has specific units.

For example, for the reaction :

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, K_c and K_p have no units.

But, the reaction,

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$, K_c has units mol L^{-1} and K_p has units bar.

However, these days we express equilibrium constant in dimensionless quantities by specifying the standard state of the reactants and the products. For example, the standard state for pure gas is 1 bar and now the partial pressures are measured with respect to this standard. Thus, a pressure of 3 bar in terms of this standard state is equal to $\frac{3 \text{ bar}}{1 \text{ bar}} = 3$, which is a dimensionless number. Similarly, for a solute, the standard state, C_o is taken as 1 molar solution and all concentrations are expressed with respect to it. The numerical value of equilibrium constant depends upon the standard state selected. Therefore, in this system both K_p and K_c become dimensionless quantities but have different numerical values because of different standard states. This is in a similar way that if we select standard height as 1 m, then a building of height 10 m may be expressed as $\frac{10 \text{ m}}{1 \text{ m}} = 10$.

SOLVED EXAMPLES

❑ **Example 2.**

At equilibrium, the concentrations of N_2, O_2 and NO in a sealed vessel at 800 K are :

$N_2 = 3.0 \times 10^{-3}$ M, $O_2 = 4.2 \times 10^{-3}$ M and $NO = 2.8 \times 10^{-3}$ M

Calculate the equilibrium constant K_c for the reaction :

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

N.C.E.R.T.

Solution: The equilibrium constant for the reaction :

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \text{ is}$$

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

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$[N_2] = 3.0 \times 10^{-3}$ M, $[O_2] = 4.2 \times 10^{-3}$ M, $[NO] = 2.8 \times 10^{-3}$ M

$$\therefore \quad K_c = \frac{(2.8\times10^{-3}\text{M})^2}{(3.0\times10^{-3}\text{M})\,(4.2\times10^{-3}\text{M})}$$

$$= \mathbf{0.622}$$

Example 3.

What is K_c for the following equilibrium, when the equilibrium concentration of each substance is $[SO_2] = 0.60$ M, $[O_2] = 0.82$ M and $[SO_3] = 1.90$ M

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

N.C.E.R.T.

Solution: The equilibrium constant, K_c is

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O^2]}$$

$[SO_2] = 0.60$ M, $[O_2] = 0.82$ M and $[SO_3] = 1.90$ M

$$K_c = \frac{(1.90\text{M})^2}{(0.60\text{M})^2(0.82\text{ M})}$$

$$= \mathbf{12.229\ M^{-1}} \text{ or } \mathbf{12.229\ mol^{-1}\ L}$$

Example 4.

PCl_5, PCl_3 and Cl_2 are at equilibrium at 500 K and having concentration 1.59 M PCl_3, 1.59 M Cl_2 and 1.41 M PCl_5. Calculate K_c for the reaction :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

N.C.E.R.T.

Solution: The equilibrium constant for the reaction may be written as :

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

$[PCl_5] = 1.41$ M, $[PCl_3] = 1.59$ M, $[Cl_2] = 1.59$ M

$$= \frac{(1.59)\,(1.59)}{1.41}$$

$$= \mathbf{1.79\ M}$$

Example 5.

An equilibrium system for the reaction between hydrogen and iodine to give hydrogen iodide at 670 K in a 5 litre flask contains 0.4 mole of hydrogen, 0.4 mole of iodine and 2.4 moles of hydrogen iodide. Calculate equilibrium constant.

Solution: For the reaction,

$$H_2(g) + I_2(g) = 2HI(g)$$

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

The molar concentrations of various species at equilibrium are :

$[H_2] = \frac{0.4}{5} = 0.08$ mol L^{-1}; $[I_2] = \frac{0.4}{5} = 0.08$ mol L^{-1};

$[HI] = \frac{2.4}{5} = 0.48$ mol L^{-1}

Substituting the various values in the above expression of K_c,

$$K = \frac{(0.48)^2}{(0.08)\,(0.08)} = \mathbf{36.0}$$

Example 6.

(i) Determine K_c for the reaction :

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$K_p = 3.4\ bar^{-1}$ *at 1000°C*

(ii) Determine K_p for the reaction :

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

$K_c = 3.75 \times 10^{-6}$ *at 1069 K*

Solution: *(i)* $K_p = K_c(RT)^{\Delta n_g}$ or $K_c = K_p(RT)^{-\Delta n_g}$

$\Delta n_g = 2 - (2 + 1) = -1$

$\therefore \quad K_c = 3.4 \times (0.083 \times 1273)^1 = \mathbf{359.24}$

(ii) $K_p = K_c(RT)^{\Delta n_g}$

$\Delta n = 2 + 1 - 2 = 1$

$K_p = 3.75 \times 10^{-6} \times (0.083 \times 1069)^1$

$= \mathbf{3.33 \times 10^{-4}}$

Example 7.

At 700 K, the equilibrium constant K_p, for the reaction

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

is 1.8×10^{-3} kPa. What is the numerical value in moles per dm^3 of K_c for the reaction at the same temperature ?

Solution: K_p and K_c are related as :

$$K_p = K_c(RT)^{\Delta n_g} \quad \text{or} \quad K_c = \frac{K_p}{(RT)^{\Delta n_g}}$$

$T = 700$ K, $R = 8.31$ J mol^{-1} K^{-1}; $\Delta n_g = (2 + 1) - 2 = 1$

$K_p = 1.8 \times 10^{-3}$ kPa $= 1.8$ Pa

$$K_c = \frac{1.8\ Pa}{[(8.31\text{J mol}^{-1}\text{ K}^{-1})\,(700\text{ K})]^1}$$

$$= \frac{1.8\ \text{Nm}^{-2}}{[(8.31\text{ Nm mol}^{-1}\text{ K}^{-1})\,(700\text{ K})]}$$

($\because$ Pa $= Nm^{-2}$, J = Nm)

$= \mathbf{3.09 \times 10^{-4}\ mol\ m^{-3}}$.

or $\mathbf{3.09 \times 10^{-7}\ mol\ dm^{-3}}$.

TYPES OF CHEMICAL EQUILIBRIUM

There are two types of chemical equilibria :

1. Homogeneous equilibrium

The equilibrium reactions in which all the reactants and the products are in the same phase are called **homogeneous equilibrium reactions.** For example,

$$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

liquid phase

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$$

liquid phase

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

gas phase

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

gas phase

2. Heterogeneous equilibrium

The equilibrium reactions in which the reactants and the products are present in

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different phases are called **heterogeneous equilibrium reactions.** For example,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

$$H_2O(l) \rightleftharpoons H_2O(g)$$

$$Ca(OH)_2(s) \overset{Water}{\rightleftharpoons} Ca^{2+}(aq) + 2OH^-(aq)$$

It may be noted that the equilibrium expression for heterogeneous reactions does not include the concentrations of pure solids because their concentrations remain constant. Similarly, the concentrations of pure liquids are also assumed to be constant and these do not appear in equilibrium concentration expression.

By convention, the concentration of all pure solids and pure liquids are taken as unity *i.e.*, [solid] = 1, [liquid] = 1.

However, when the substance occurs in liquid solutions, their concentrations are variable and therefore, their concentrations are given in equilibrium expression. For example, consider the heterogeneous reaction,

$$CaCO_3(s) \overset{Heat}{\rightleftharpoons} CaO(s) + CO_2(g)$$

$$K = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$$

The concentrations of $CaO(s)$ and $CaCO_3(s)$ may be assumed to be constant, *i.e.*, $[CaO(s)] = 1$ and $[CaCO_3(s)] = 1$ so that

$$K = [CO_2(g)]$$

Since the partial pressure of a gaseous component is proportional to its concentration,

$$K_p = p(CO_2)$$

This shows that at a particular temperature for the decomposition of calcium carbonate, the equilibrium partial pressure of CO_2 system is equal to K_p. This relation gives us a very easy way to measure K_p. For this, we measure simply the pressure of CO_2 in equilibrium with $CaO(s)$ and $CaCO_3(s)$ at a particular temperature. For example, it has been found that at 1100 K, the pressure of CO_2 in equilibrium with $CaCO_3(s)$ and $CaO(s)$ is 2.0×10^5 Pa. Therefore, equilibrium constant at 1100 K for the above reaction is :

$$K_p = p(CO_2) = 2.0 \times 10^5 \text{ Pa}$$

Similarly, consider the reaction :

$Ni(s) + 4\,CO(g) \rightleftharpoons Ni(CO)_4(g)$

The equilibrium constant may be written as :

$$K_c = \frac{[Ni(CO)_4]}{[CO]^4}$$

It may be noted that *the pure substances (solids or liquids) must be present for the equilibrium to exist, but they do not appear in the expression for the equilibrium constant.* Thus, when we write the equilibrium constant for a reaction involving pure solids and liquids, we ignore these. Similarly, for the reaction:

$$Ag_2O(s) + 2HNO_3(aq) \rightleftharpoons 2AgNO_3(aq) + H_2O(l)$$

$$K_c = \frac{[AgNO_3]^2}{[HNO_3]^2}$$

Equilibrium Constant Expressions for Some Reactions

Before writing the equilibrium constant expressions, the following facts must be remembered:

1. For heterogeneous reactions, the equilibrium expressions do not include the concentration of pure solids and pure liquids. By **convention,** [solid] = 1 and [liquid] = 1.

2. If concentration of solvent is used, it is considered as constant because it is present in large quantity and will not change appreciably. For example, consider the reaction :

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The equilibrium constant may be written as

$$K = \frac{[NH_4^+(aq)]\,[OH^-(aq)]}{[NH_3(aq)]\,[H_2O(l)]}$$

Water is present in large quantity and will not change appreciably during the reaction. By convention, we write $[H_2O]$ = constant, so that

$$K[H_2O] = \frac{[NH_4^+(aq)]\,[OH^-(aq)]}{[NH_3(aq)]} = K'$$

Generally, the prime on K is not written *i.e.*,

$$K = \frac{[NH_4^+(aq)]\,[OH^-(aq)]}{[NH_3(aq)]}$$

Let us write the equilibrium constant expressions for some reactions :

(*i*) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$$K = \frac{[NO(g)]^2}{[N_2(g)]\,[O_2(g)]}$$ **(No units)**

(*ii*) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$K = \frac{[PCl_3(g)]\,[Cl_2(g)]}{[PCl_5(g)]}$$ **(Units = mol L^{-1})**

(*iii*) $CrO_4^{2-}(aq) + Pb^{2+}(aq) \rightleftharpoons PbCrO_4(s)$

$$K = \frac{[PbCrO_4(s)]}{[CrO_4^{2-}(aq)]\,[Pb^{2+}(aq)]}$$

Now, $[PbCrO_4(s)] = 1$

$$K = \frac{1}{[CrO_4^{2-}(aq)]\,[Pb^{2+}(aq)]}$$

(Units = mol^{-2} L^2)

(*iv*) $2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$

$$K = \frac{[NO_2(g)]^4[O_2(g)]}{[N_2O_5(g)]^2}$$

(Units = mol^3 L^{-3})

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(v) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

$$K = \frac{[Fe_3O_4(s)]\,[H_2(g)]^4}{[Fe(s)]^3\,[H_2O(g)]^4}$$

By convention, $[Fe_3O_4(s)] = 1$ and $[Fe(s)] = 1$ so that

$$K = \frac{[H_2(g)]^4}{[H_2O(g)]^4} \qquad \textbf{(No units)}$$

Equilibrium Constant Expressions in terms of Partial Pressures

Equilibrium constant (K_p) in terms of partial pressures of substances may be written as :

(i) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$K_p = \frac{(p_{NO_2})^2}{(p_{N_2O_4})} \qquad \textbf{(Units = atm)}$$

(ii) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$K_p = \frac{(p_{PCl_3})\,(p_{Cl_2})}{p_{PCl_5}} \qquad \textbf{(Units = atm)}$$

(iii) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

$$K_p = \frac{(p_{H_2})\,(p_{I_2})}{(p_{HI})^2} \qquad \textbf{(No units)}$$

(iv) $SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$

$$K_p = \frac{(p_{NO})\,(p_{SO_3})}{(p_{SO_2})\,(p_{NO_2})} \qquad \textbf{(No units)}$$

SOLVED EXAMPLES

❑ **Example 8.**

Write the equilibrium constant expressions for the following reactions :

(a) $BaCO_3(s) \rightleftharpoons BaO(s) + CO_2(g)$

(b) $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$

(c) $CH_3COCH_3(l) \rightleftharpoons CH_3COCH_3(g)$

(d) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$

(e) $Al(s) + 3H^+(aq) \rightleftharpoons Al^{3+}(aq) + 3/2\ H_2(g)$

(f) $HPO_4^{2-}(aq) + H_2O \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$

Solution:

(a) $BaCO_3(s) \rightleftharpoons BaO(s) + CO_2(g)$

$$K = \frac{[BaO(s)]\,[CO_2(g)]}{[BaCO_3(s)]}$$

By convention, $[BaO(s)] = 1$ and $[BaCO_3(s)] = 1$

$\therefore$ $K = [CO_2(g)]$ or $K_p = p(CO_2)$

(b) $AgBr\,(s) \rightleftharpoons Ag^+\,(aq) + Br^-\,(aq)$

$$K = \frac{[Ag^+(aq)]\,[Br^-(aq)]}{[AgBr(s)]}$$

or $K = [Ag^+\,(aq)]\,[Br^-(aq)]$ $\quad (\because [AgBr\,(s)] = 1)$

(c) $CH_3COCH_3(l) \rightleftharpoons CH_3COCH_3(g)$

$$K = \frac{[CH_3COCH_3(g)]}{[CH_3COCH_3(l)]} \text{ or } = [CH_3COCH_3(g)]$$

$(\because [CH_3COCH_3(l)] = 1)$

(d) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$

$$K = \frac{[CO_2(g)]\,[H_2O(l)]^2}{[CH_4(g)]\,[O_2(g)]^2} \text{ or } = \frac{[CO_2(g)]}{[CH_4(g)]\,[O_2(g)]^2}$$

$(\because [H_2O(l)] = 1)$

(e) $Al(s) + 3H^+(aq) \rightleftharpoons Al^{3+}(aq) + \frac{3}{2}H_2(g)$

$$K = \frac{[Al^{3+}(aq)]\,[H_2(g)]^{3/2}}{[Al(s)]\,[H^+(aq)]^3}$$

or $$= \frac{[Al^{3+}(aq)]\,[H_2(g)]^{3/2}}{[H^+(aq)]^3} \qquad (\because [Al(s)] = 1)$$

(f) $HPO_4^{2-}(aq) + H_2O \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$

$$K = \frac{[H_3O^+(aq)]\,[PO_4^{3-}(aq)]}{[HPO_4^{2-}(aq)]\,[H_2O]}$$

or $$= \frac{[H_3O^+(aq)]\,[PO_4^{3-}(aq)]}{[HPO_4^{2-}(aq)]}$$

❑ **Example 9.**

The equilibrium constant for a gaseous reaction is

$$K_c = \frac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression. **N.C.E.R.T.**

Solution: The chemical equation is :

$4NO\,(g) + 6H_2O\,(g) \rightleftharpoons 4NH_3(g) + 5O_2\,(g)$

❑ **Example 10.**

Which of the following reactions involve homogeneous equilibrium and which involve heterogeneous equilibrium ?

(a) $2N_2O\,(g) \rightleftharpoons 2N_2(g) + O_2(g)$

(b) $2NH_3\,(g) \rightleftharpoons N_2(g) + 3H_2(g)$

(c) $2Cu(NO_3)_2\,(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

(d) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH\,(aq)$

(e) $Fe^{3+}\,(aq) + 3OH^-\,(aq) \rightleftharpoons Fe(OH)_3\,(s)$

Solution:

(a) Homogeneous equilibrium

(b) Homogeneous equilibrium

(c) Heterogeneous equilibrium

(d) Homogeneous equilibrium

(e) Heterogenous equilibrium

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❑ **Example 11.**

Write the expression for the equilibrium constant, K_c for each of the following reactions :

(a) $2NOCl\,(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

(b) $2Cu(NO_3)_2\,(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

(c) $CH_3COOC_2H_5 \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$

(d) $Fe^{3+}\,(aq) + 3OH^-\,(aq) \rightleftharpoons Fe(OH)_3(s)$

(e) $I_2(s) + 5F_2(g) \rightleftharpoons 2IF_5(g)$

Solution:

(a) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

$$K_c = \frac{[NO]^2\,[Cl_2]}{[NOCl]^2}$$

(b) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

$$K_c = [NO_2]^4[O_2]$$

(c) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH\,(aq)$

$$K_c = \frac{[CH_3COOH]\,[C_2H_5OH]}{[CH_3COOC_2H_5]}$$

(d) $Fe^{3+}\,(aq) + 3OH^-\,(aq) \rightleftharpoons Fe(OH)_3(s)$

$$K_c = \frac{1}{[Fe^{3+}]\,[OH^-]^3}$$

(e) $I_2(s) + 5F_2(g) \rightleftharpoons 2IF_5(g)$

$$K_c = \frac{[IF_5]^2}{[F_2]^5}$$

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

The important characteristics of equilibrium constant are :

1. *Equilibrium constant is applicable only when the concentrations of reactants and products have attained their equilibrium state.*

2. *The value of equilibrium constant is independent of the original concentration of reactants.* For example, the equilibrium constant for the reaction,

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

at 298 K is :

$$K = \frac{[FeSCN^{2+}]}{[Fe^{3+}]\,[SCN^-]} = 138.0\ L\ mol^{-1}$$

Whatever may be the initial concentrations of the reactants, Fe^{3+} and SCN^- ions, the value of K comes out to be 138.0 L mol^{-1} at 298 K.

3. *The equilibrium constant has a definite value for every reaction at a particular temperature.* However, it varies with change in temperature. For example, the equilibrium constant for the reaction between hydrogen and iodine to form hydrogen iodide is 48 at 717 K.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K = \frac{[HI]^2}{[H_2]\,[I_2]} = 48$$

For this reaction, the value of K is fixed as long as the temperature remains constant.

4. *For a reversible reaction, the equilibrium constant for the forward reaction is inverse of the equilibrium constant for the backward reaction.* For example, if equilibrium constant, K, for the reaction of combination between hydrogen and iodine at 717 K is 48

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K = \frac{[HI]^2}{[H_2]\,[I_2]} = 48$$

Then, the equilibrium constant for the decomposition of hydrogen iodide (K′) is the inverse of the above equilibrium constant.

$$2HI\,(g) \rightleftharpoons H_2(g) + I_2(g)$$

$$K' = \frac{[H_2]\,[I_2]}{[HI]^2}$$

$$= \frac{1}{K} = \frac{1}{48} = 0.02$$

In general,

$$K_{forward\ reaction} = \frac{1}{K_{backward\ reaction}}$$

5. *The equilibrium constant is independent of the presence of catalyst.* This is so because the catalyst affects the rates of forward and backward reactions equally.

EQUILIBRIUM CONSTANT AND THE CHEMICAL EQUATION

It must be remembered that the magnitude of equilibrium constant depends on the equation written for the reaction. If we change the stoichiometric coefficients in a chemical reaction by multiplying or dividing throughout by a factor, then we must make sure that the expression for equilibrium constant also shows that change. Thus, the appropriate equation must be specified when an equilibrium constant is stated.

Suppose we write the equilibrium constant for the reaction,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

or $$K = \frac{[HI]^2}{[H_2]\,[I_2]} = x$$

(*i*) The equilibrium constant for the reverse reaction :

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

at the same temperature is

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$$K_1 = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{x} \text{ or } = \frac{1}{K}$$

Thus, $K_1 = \frac{1}{K}$

Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the forward direction.

(*ii*) If the equation is divided by 2 *i.e.,* if the reaction is written as :

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

The equilibrium constant for the above reaction is

$$K_2 = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} = \left[\frac{[HI]^2}{[H_2][I_2]}\right]^{1/2} = x^{1/2}$$

or $K_2 = x^{\frac{1}{2}} = K^{1/2}$

(*iii*) If the equation is mulitiplied by 2 *i.e.,* if the reaction is

$$2H_2(g) + 2I_2(g) \rightleftharpoons 4HI(g)$$

$$K_3 = \frac{[HI]^4}{[H_2]^2[I_2]^2} = \left[\frac{[HI]^2}{[H_2][I_2]}\right]^2 = x^2$$

or $= (K)^2$

Similarly if the equation is multiplied by n, we get

$$n(H_2)(g) + nI_2(g) \rightleftharpoons 2nHI(g)$$

$$K_4 = \frac{[HI]^{2n}}{[H_2]^n[I_2]^n} = K^n$$

(*iv*) If the equation is written in two steps then the equilibrium constant is product of the equilibrium constants of individual steps.

For example, consider the reaction :

$$N_2 + 2O_2 \rightleftharpoons 2NO_2$$

For the reaction

$$K = \frac{[NO_2]^2}{[N_2][O_2]^2}$$

Suppose the reaction occurs in two steps as :

(*i*) $N_2 + O_2 \rightleftharpoons 2NO$

(*ii*) $2NO + O_2 \rightleftharpoons 2NO_2$

For (*i*) step $K_1 = \frac{[NO]^2}{[N_2][O_2]}$

For (*ii*) step $K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$

Now $K_1 \times K_2 = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]}$

$$= \frac{[NO_2]^2}{[N_2][O_2]^2} = K$$

$\therefore$ $K = K_1 \times K_2$

For example,

$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$

$$K_1 = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = 138 \text{ at } 298 \text{ K}$$

However, if we write the equation as :

$2Fe^{3+}(aq) + 2\,SCN^-(aq) \rightleftharpoons 2FeSCN^{2+}(aq)$

$$\text{then } K_2 = \frac{[FeSCN^{2+}]^2}{[Fe^{3+}]^2[SCN^-]^2}$$

$$= K_1^2 = (138)^2 = 19044$$

Again, for the reaction,

$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$

$$K_1 = \frac{[Cu^{2+}(aq)]}{[Ag^+(aq)]^2} = 2 \times 10^{15} \text{ at } 298 \text{ K}$$

However, if we write,

$$\frac{1}{2}Cu(s) + Ag^+(aq) \rightleftharpoons \frac{1}{2}Cu^{2+}(aq) + Ag(s)$$

$$K_2 = \frac{[Cu^{2+}(aq)]^{1/2}}{[Ag^+(aq)]} = K_1^{1/2} = (2 \times 10^{15})^{1/2}$$

$$= \mathbf{4.5 \times 10^7 \text{ at } 298 \text{ K.}}$$

TO SUM UP

1. When the coefficients of a given reaction equation are multiplied by $\frac{1}{2}$, then the K for the new reaction equation is the square root of K. For example,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \text{ at } 717 \text{ K}_1 = 48$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

$$K_2 = \sqrt{48} = 6.93$$

2. When the coefficients of a given reaction equation are doubled, then the K for the new equation is the square of the original K. For example,

$$H_2(s) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K_1 = 48 \text{ at } 717 \text{ K}$$

$$2H_2(g) + 2I_2(g) \rightleftharpoons 4HI(g)$$

$$K_3 = (48)^2 = 2304$$

In general, when we multiply the terms in an equation by a certain value, we must change the K, for the equation to a power equal to that value.

$$\mathbf{nH_2(g) + nI_2(g) \rightleftharpoons 2nHI(g); \quad K_4 = (K)^n}$$

e.g., if $n = \frac{1}{2}$, $K_4 = (K)^{1/2}$ or $\sqrt{K}$ and if $n = 2$, $K_4 = (K)^2$

3. When a given reaction equation is reversed, then the K for the reverse reaction equation is the reciprocal of the K for the original equation.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \text{ at } 717 \text{ K};$$

$$K = 48$$

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$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

$$K = \frac{1}{48} = 0.0208$$

Thus, the relation between equilibrium constants for a general reaction and its multiples are :

$$aA + bB \rightleftharpoons cC + dD \qquad K$$

$$cC + dD \rightleftharpoons aA + bB \qquad K_1 = \frac{1}{K}$$

$$naA + nbB \rightleftharpoons ncC + ndD \qquad K_2 = K^n$$

Temperature Dependence of Equilibrium Constant

The temperature dependence of equilibrium constant is given by the expression :

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where K_1 and K_2 are the equilibrium constants at temperatures T_1 and T_2 respectively and ΔH is the enthalpy change for the reaction. It is assumed that ΔH is independent of temperature.

This is known as **van't Hoff equation**.

We may conclude from this equation that

(*i*) If $\Delta H = 0$ *i.e.* no heat is evolved or absorbed in the reaction,

$$\log \frac{K_2}{K_1} = 0 \qquad \text{or} \qquad \frac{K_2}{K_1} = 1$$

$$\therefore \quad K_2 = K_1$$

This means that *equilibrium constant does not change with temperature.*

(*ii*) If $\Delta H = +ve$ *i.e.* heat is absorbed in the reaction (endothermic reaction), then

$$\log \frac{K_2}{K_1} = +\text{ve} \qquad \text{or } \log K_2 > \log K_1$$

$$\therefore \quad K_2 > K_1$$

This means that *equilibrium constant increases with increase in temperature.*

(*iii*) If $\Delta H = -ve$ *i.e.* heat is evolved in the reaction (exothermic reaction), then

$$\log \frac{K_2}{K_1} = -\text{ve} \qquad \text{or } \log K_2 < \log K_1$$

$$\therefore \quad K_2 < K_1$$

This means that *equilibrium constant decreases with increase in temperature.*

❑ **Example 12.**

K_p for the reaction :

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is 2.5×10^{10}. Calculate the K_p values for the following reactions:

(i) $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

(ii) $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$

(iii) $3SO_2(g) + \frac{3}{2}O_2(g) \rightleftharpoons 3SO_3(g)$

Solution: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$K_p = 2.5 \times 10^{10}$

(*i*) $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

$$K_i = (K_p)^{1/2} = (2.5 \times 10^{10})^{1/2} = 1.58 \times 10^5$$

(*ii*) $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$

$$K_{ii} = \frac{1}{K_i} = \frac{1}{1.58 \times 10^5} = 6.3 \times 10^{-6}$$

(*iii*) $3SO_2(g) + \frac{3}{2}O_2(g) \rightleftharpoons 3SO_3(g)$

$$K_{iii} = (K_p)^{3/2} = (2.5 \times 10^{10})^{3/2} = 3.95 \times 10^{15}$$

Practice Problems

1. For the formation of NH_3 from N_2 and H_2, the following concentrations were obtained at equilibrium at 500 K :
$[N_2] = 1.5 \times 10^{-2}$ M, $[H_2] = 3.0 \times 10^{-2}$ M and $[NH_3] = 1.2 \times 10^{-2}$ M
Calculate the equilibrium constant. ***N.C.E.R.T.***

2 At equilibrium for the reaction :
$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$
a 10 L reaction vessel was found to contain 2.5×10^{-3} mol of H_2, 0.150 mol of HBr and 2.8×10^{-3} mol of Br_2. What is the value of K at this temperature ?

3 Nitrogen chloride (NOCl) decomposes into NO and Cl_2 as :
$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$
The equilibrium partial pressures of NOCl, NO and Cl_2 at 500 K have been found to be 0.75, 0.11 and 0.84 atm respectively. Calculate K_p for the reaction.

4. For the reaction $N_2 + 2O_2 \rightleftharpoons 2NO_2$ the equilibrium concentrations in a 1.5 L reaction vessel are 5.0 mol of N_2, 7.0 mol of O_2 and 0.10 mol of NO_2 at a certain temperature. Calculate the equilibrium constant.

5. Write the relationship between K_p and K_c for the reaction :
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

6. K_p for the reaction
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.157 atm at 27°C and 1 atm pressure. Calculate K_c for the reaction.

7. At 800 K, the equilibrium constant for the reaction,
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 6.05×10^{-2} L^2 mol^{-2}. Calculate K_p for the reaction at the same temperature.

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8. Write the expression for equilibrium constant, K for each of the following :

(*i*) $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$

(*ii*) $Na_2CO_3(s) + SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons Na_2SO_4(s) + CO_2(g)$

(*iii*) $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

9. Write the equilibrium constant expressions for the following reactions :

(*i*) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$

(*ii*) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$

10. The equilibrium constant for the reaction

$I_2(g) + Cl_2(g) \rightleftharpoons 2ICl(g)$

at 740 K is 640. What is the equilibrium constant for the reaction ?

$2ICl(g) \rightleftharpoons I_2(g) + Cl_2(g)$

at the same temperature.

11. For the reaction,

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

At 400 K, $K_p = 41$. Find the value of K_p for each of the following reactions at the same temperature :

(*i*) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

(*ii*) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$

(*iii*) $2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$

12. The value of K_p for the reaction at 500 K :

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ is 1.8×10^{-2} bar^{-1}.

Calculate K_c for reaction at this temperature.

N.C.E.R.T.

13. For the reaction

$2A(g) + 2B_2(g) \rightleftharpoons 2AB_2(g)$

the equilibrium constant K_p at 27°C is 4.0. What is the value of K_p for

(*a*) $2AB_2(g) \rightleftharpoons 2A(g) + 2B_2(g)$

(*b*) $A(g) + B_2 \rightleftharpoons AB_2(g)$

14. Write the relationship between equilibrium constants for the following reactions :

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

$4NO_2(g) \rightleftharpoons 4NO(g) + 2O_2(g)$

15. The equilibrium constant for the reaction :

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

is 256 at 1000 K. What is the value of K for the reaction :

$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$ at the same temperature.

Answers to Practice Problems

1. 3.56×10^2 **2.** 3.21×10^3

3. 0.0181 **4.** 6.12×10^{-5}

5. $K_p = K_c/RT$ **6.** 6.37×10^{-3} mol L^{-1}.

7. 1.40×10^{-5} atm^{-2}.

8. (*i*) $\frac{[CO(g)]^2}{[CO_2(g)]}$ (*ii*) $\frac{[CO_2(g)]}{[SO_2(g)]\,[O_2(g)]^{1/2}}$

(*iii*) $[Pb^{2+}(aq)]\,[I^-(aq)]^2$

10. 1.56×10^{-3} **11.** (*i*) 0.024 (*ii*) 6.4 (*iii*) 1681

12. 4.33×10^{-4} **13.** (*a*) 0.25 (*b*) 2

14. $K_2 = \frac{1}{K_1^2}$ **15.** 6.25×10^{-2}

Hints & Solutions on page 94

APPLICATIONS OF EQUILIBRIUM CONSTANT

1. Predicting the Extent of a Reaction

The magnitude of equilibrium constant K indicates the extent to which a reaction can go. However, it may be noted that an equilibrium does not give any information about the rate at which the equilibrium is reached.

As we know, the magnitude of K_c or K_p is directly proportional to the concentration of products (because these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (because these appear in the **denominator**). This implies that a high value of K means higher concentrations of products (or low concentrations of reactants) and vice versa. Thus, **larger the value of K, the greater will be the equilibrium concentration of the products relative to those of the reactants *i.e.*, the reaction proceeds to a greater extent.**

For example, consider the reaction

$2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$

The equilibrium constant for the reaction at 298 K is

$$K = \frac{[N_2][O_2]^2}{[NO_2]^2} = 6.7 \times 10^{-16} \text{ mol L}^{-1}$$

The value of K is very small which means that the molar concentrations of N_2 and O_2 in the equilibrium mixture are small. In other words, the forward reaction has proceeded to small extent only. Thus we can say that NO_2 is quite stable and decomposes only slightly.

Let us consider another reaction,

$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$

The equilibrium constant for the reaction at 1000 K is :

$$K = \frac{[CO_2]^2}{[CO]^2\,[O_2]} = 2.3 \times 10^{22} \text{ mol L}^{-1}$$

For this reaction, the value of K is very large, which means that the molar concentration of CO_2 in the equilibrium mixture is quite large and the molar concentrations of CO and O_2 are very small. Thus, the reaction goes almost to completion and it may be concluded that carbon dioxide is more stable than carbon monoxide and oxygen under these conditions.

We can make the following **generalizations** concerning the composition of equilibrium mixture and equilibrium constant K (K_c or K_p) :

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• **If $K > 10^3$, products predominate over reactants at equilibrium. If K is very large, the reaction proceeds nearly to completion.**

For example, the following reactions proceed nearly to completion :

(*i*) Reaction of H_2 and O_2 at 500 K having very large equilibrium constant :

$$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g) \quad K_c = 2.4 \times 10^{47}$$

(*ii*) Reaction of H_2 and Cl_2 at 300 K.

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) \quad K_c = 4.0 \times 10^{31}$$

(*iii*) Reaction of H_2 and Br_2 at 300 K

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr_2(g) \quad K_c = 5.4 \times 10^{18}$$

• **If $K < 10^{-3}$, reactants predominate over products. If K is very small, the reaction proceeds to very small extent or rarely .**

For example, the following reactions proceed to very small extent :

(*i*) The reaction between N_2 and O_2 has very low equilibrium constant :

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad K_c = 4.8 \times 10^{-31}$$

(*ii*) The decomposition of water into H_2 and O_2 at 500 K has very small equilibrium constant :

$$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g) \quad K_c = 4.1 \times 10^{-48}$$

• **If K is in the range of 10^{-3} to 10^3 appreciable concentrations of both reactants and products are present.**

For example :

(*i*) The reaction of H_2 and I_2 to give HI at 700 K has intermediate value of equilibrium constant :

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad K = 57.0$$

(*ii*) The gas phase decomposition of N_2O_4 to NO_2 at 298 K has also equilibrium constant value, which is neither to small nor to large.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_c = 4.64 \times 10^{-3}$$

The equilibrium mixture contains appreciable concentrations of both N_2O_4 and NO_2

These generalization are illustrated in Fig. 11.

Let us compare two similar reactions :

(i) $Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$

$$K = \frac{[Cu^{2+}(aq)]}{[Ag^+(aq)]^2} = 2.0 \times 10^{15} \text{ at 298 K.}$$

($\because$ [Cu(*s*)] and [Ag(*s*)] = 1)

(*ii*) $Cu(s) + Zn^{2+}(aq) \rightleftharpoons Zn(s) + Cu^{2+}(aq)$

$$K = \frac{[Cu^{2+}(aq)]}{[Zn^{2+}(aq)]} = 2.0 \times 10^{-19} \text{ at 298 K.}$$

($\because$ [Cu(*s*)] and [Zn(*s*)] = 1)

The comparison of K values of two reactions shows that the second reaction is not possible. In other words, Ag will be precipitated by Cu when a copper rod is dipped in a solution containing Ag^+ ions, but zinc will not be precipitated by Cu when copper rod is dipped in Zn^{2+} solution. In fact, the reverse reaction is possible in the second case. The equilibrium constant for the reverse reaction,

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Cu(s) + Zn^{2+}(aq)$$

will be $K' = \frac{1}{K} = \frac{1}{2.0 \times 10^{-19}} = 5.0 \times 10^{18}$ at 298 K.

Thus, when a zinc rod is dipped in a solution containing Cu^{2+} ions, Cu will be precipitated.

2. Predicting the Direction of the Reaction

The equilibrium constant also helps to find the direction in which an arbitrary reaction mixture of reactants and products will proceed. For this purpose, we calculate the **reaction quotient** Q. The reaction quotient is the ratio of product of concentrations (or partial pressures) of products to that of the reactants at any stage of the reaction. In other words, the reaction quotient is defined in the same way as the equilibrium constant with molar concentrations to give Q_c or with partial pressures to give Q_p. For example,

$$aA + bB \rightleftharpoons cC + dD$$

$$Q_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

or

$$Q_p = \frac{\left(p_C{}^c\right)\left(p_D{}^d\right)}{\left(p_A{}^a\right)\left(p_B{}^b\right)}$$

At equilibrium, $Q_c = K_c$

Thus,

- if $Q_c > K_c$, the reaction will proceed from right to left i.e., in the direction of reactants (**reverse reaction**).

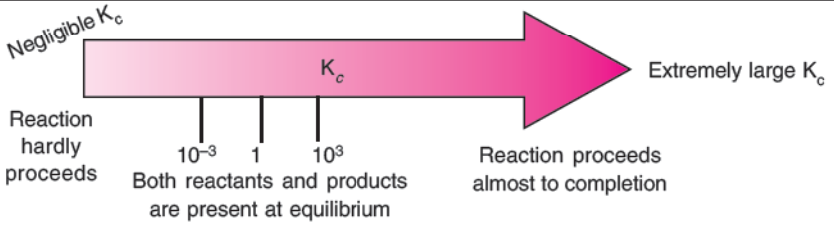

Fig. 11. Dependence of extent of reaction on equilibrium constant.

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- if $Q_c < K_c$, the reaction will proceed from left to right i.e., in the direction of the products (**forward reaction**).
- if $Q_c = K_c$, the reaction mixture is already **at equilibrium** and no reaction occurs.

Thus, **a reaction has a tendency to form products if Q < K and to form reactants if Q > K.**

This has also been shown in Fig. 12.

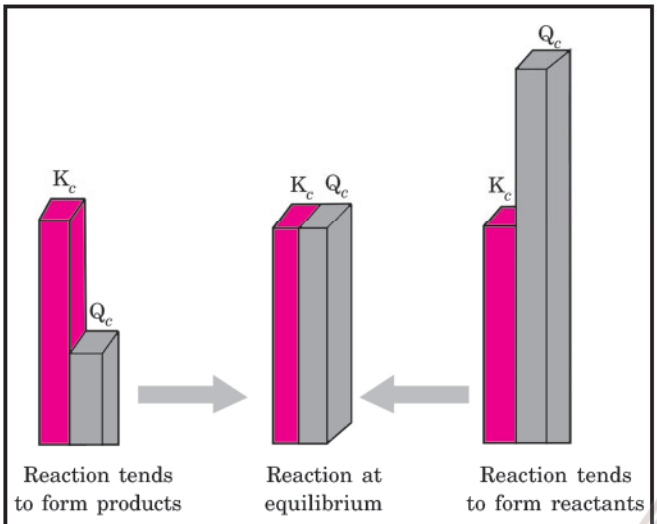

Fig. 12. Relation between K_c and Q_c and the direction of the reaction.

For example, in the reaction,

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ the molar concentrations of H_2, I_2 and HI are 0.1, 0.2 and 0.4 mol L^{-1} respectively at 700 K. The reaction quotient at this stage of the reaction is,

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$$

Now, K_c for the reaction at 700 K is 57.0 Since $Q_c < K$, the reaction is not at equilibrium. It will move towards right *i.e,*. more of $H_2(g)$ and $I_2(g)$ will react to form HI (g) and their concentrations will decrease till Q_c becomes equal to K_c.

3. Calculation of Equilibrium Constants and Concentration.

If the concentration of reactants and products are known at equilibrium in a reaction, the equilibrium constant can be calculated. On the other hand, if the equilibrium constant is known, the concentrations in the equilibrium mixture can be calculated.

The equilibrium concentrations can be calculated by the following steps :

Step 1. Write the balanced chemical equation for the reaction.

Step 2. Under the balanced equation set up a table that lists for each species involved in the reaction :

(i) the initial concentration or partial pressure of each species,

(ii) the change in concentration on going to equilibrium and

(iii) the equilibrium concentration.

For this, we write x as the concentration of one of the substance that reacts on going to the equilibrium. Then use the stoichiometry of the reaction to determine the concentration of the other substances in terms of x.

Step 3. Write the equilibrium constant expression for the reaction and substitute the equilibrium concentrations in it. Then solve for x. If need be solve a quadratic equation.

Step 4. Calculate the equilibrium concentrations from the calculated value of x.

Step 5. Check your results by substituting them into the equilibrium equation.

These can be understood while solving numerical problems.

❑ **Example 13.**

A mixture of H_2, N_2 and NH_3 with molar concentrations 5.0×10^{-3} mol L^{-1}, 4.0×10^{-3} mol L^{-1} and 2.0×10^{-3} mol L^{-1} respectively was prepared and heated to 500 K. The value of K_c for the reaction : $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ at this temperature is 60.

Predict whether ammonia tends to form or to decompose at this stage of concentration.

Solution: Reaction quotient, Q_c for the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$[NH_3] = 2.0 \times 10^{-3}$ mol L^{-1}, $[H_2] = 5.0 \times 10^{-3}$ mol L^{-1}

$[N_2] = 4.0 \times 10^{-3}$ mol^{-1}

$$Q_c = \frac{(2.0 \times 10^{-3})^2}{(4.0 \times 10^{-3})(5.0 \times 10^{-3})^3} = 8.0 \times 10^3$$

$K_c = 60$

Since $Q_c > K_c$, reaction will go in the left direction and ammonia will decompose.

❑ **Example 14.**

At a certain temperature and a total pressure of 10^5 Pa, iodine vapour contain 40% by volume of iodine atoms.

$$I_2(g) \rightleftharpoons 2I(g)$$

Calculate K_p for the equilibrium.

N.C.E.R.T.

Solution: Partial pressure of I atoms,

$$p_1 = \frac{10^5 \times 40}{100} = 0.4 \times 10^5 \text{ Pa}$$

Partial presssure of I_2, $= \frac{10^5 \times 60}{100} = 0.6 \times 10^5$ Pa

$$K_p = \frac{p_I^2}{p_{I_2}} = \frac{(0.4 \times 10^5)^2}{0.6 \times 10^5} = \mathbf{2.67 \times 10^4.}$$

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Example 15.

One mole of H_2O and one mole of CO were heated in a 10 litre closed vessel at 725 K. At equilibrium, 40 per cent of water was found to react according to the equation :

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Calculate the equilibrium constant for the reaction.

N.C.E.R.T.

Solution: The reaction is

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Number of moles of water initially present= 1 mol

Percentage of water reacted = 40%

$$\therefore \quad \text{Moles of water reacted} = \frac{1 \times 40}{100} = 0.4 \text{ mol}$$

Moles of water left unreacted=1.0 – 0.4 = 0.6 mol

According to the above equation, for every one mole of H_2O, one mole of CO reacts and forms one mole each of CO_2 and H_2. Therefore,0.4 mole of H_2O will react with 0.4 mole of CO to give 0.4 mole of H_2 and 0.4 mole of CO_2. Since the total volume is 10 L, the molar concentrations at equilibrium are :

$$[H_2] = \frac{0.4}{10} \text{ mol L}^{-1}, \quad [CO_2] = \frac{0.4}{10} \text{ mol L}^{-1}$$

$$[H_2O] = \frac{0.6}{10} \text{ mol L}^{-1}, \quad [CO] = \frac{0.6}{10} \text{ mol L}^{-1}$$

$$\text{Now, } K = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{\left(\frac{0.4}{10}\right) \times \left(\frac{0.4}{10}\right)}{\left(\frac{0.6}{10}\right) \times \left(\frac{0.6}{10}\right)} = \mathbf{0.444}$$

Example 16.

The reaction :

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

is at equilibrium at 1300 K in a one litre flask. The gaseous equilibrium mixture contains 0.30 mol of CO, 0.10 mol of H_2 and 0.020 mol of H_2O and an unkown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium consant K_c for the reaction at given temperature is 3.90.

Solution: $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

$[CO] = 0.30 \text{ mol L}^{-1}$, $[H_2] = 0.10 \text{ mol L}^{-1}$, $[H_2O] = 0.020 \text{ mol L}^{-1}$ and $K_c = 3.90$

$$\therefore \quad 3.90 = \frac{[CH_4] \times 0.020}{(0.30)(0.10)^3}$$

$$\text{or} \quad [CH_4] = \frac{3.90 \times 0.30\,(0.10)^3}{0.020}$$

$$= \mathbf{0.0585.}$$

Example 17.

The equilibrium constant for the reaction : $N_2(g) + 3H_2(g) = 2NH_3(g)$ at 715 K is 6.0×10^{-2}. If in a particular reaction, there are 0.25 mol L^{-1} of H_2 and 0.06 mol L^{-1} of NH_3 present, calculate the concentration of N_2 at equilibrium.

Solution: For the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 6.0 \times 10^{-2}$$

The concentrations at equilibrium are :

$[H_2] = 0.25 \text{ mol L}^{-1}$, $[NH_3] = 0.06 \text{ mol L}^{-1}$

$$\therefore \quad K = \frac{(0.06)^2}{(0.25)^3\,[N_2]} = 6.0 \times 10^{-2}$$

$$\text{or} \quad [N_2] = \frac{(0.06)^2}{(0.25)^3\,(6.0 \times 10^{-2})} = \mathbf{3.84 \text{ mol L}^{-1}}$$

Example 18.

The equilibrium constant for the reaction

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

at 1024 K is 1.6×10^5. Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K. **N.C.E.R.T.**

Solution:

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$$

$$K = \frac{1}{1.6 \times 10^5}$$

Let at equilibrium, the pressure of HBr is decreased by p bar so that

	$2HBr(g)$	$\rightleftharpoons$	$H_2(g)$	+	$Br_2(g)$
Initial conc.	10		0		0
At. equi.	10–p		$p/2$		$p/2$

$$\therefore \quad K_p = \frac{(pH_2)\,(pBr_2)}{(pHBr)^2}$$

$$= \frac{\left(\frac{p}{2}\right) \times \left(\frac{p}{2}\right)}{(10-p)^2} = \frac{1}{1.6 \times 10^5}$$

$$\text{or} \quad \frac{p^2}{4(10-p)^2} = \frac{1}{1.6 \times 10^5}$$

Taking square root of both sides, we get

$$\frac{p}{2\,(10-p)} = \frac{1}{4 \times 10^2}$$

$$4 \times 10^2 p = 20 - 2p$$

$$\text{or} \quad 402p = 20$$

$$\therefore \quad p = \frac{20}{402} = 4.98 \times 10^{-2} \text{ bar}$$

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Hence at equilibrium,

$$pH_2 = \frac{4.98\times10^{-2}}{2} = 2.49\times10^{-2}\text{ bar}$$

$$pBr_2 = \frac{4.98\times10^{-2}}{2} = 2.49\times10^{-2}\text{ bar}$$

$$p\text{HBr} = 10 - 4.98\times10^{-2} = \mathbf{10\text{ bar.}}$$

❑ Example 19.

The equilibrium constant for the reaction :

$$H_2(g) + I_2(s) \rightleftharpoons 2\text{HI}(g)$$

is 0.35 at 298 K. In the following mixture at 298K, has equilibrium been reached ? If not, state on which side of the equilibrium, the system is :

(*i*) pH_2 = 0.10 atm and pHI = 0.80 atm; there is solid I_2 in the container.

(*ii*) pH_2 = 5.5 atm and pHI = 0.44 and there is solid I_2 in the container.

(*iii*) pH_2 = 2.5 atm and pH = 0.15 atm and there is solid I_2 in the container.

Solution: $H_2(g) + I_2(g) \rightleftharpoons 2\text{HI}(g)$

Since there is solid iodine $I_2(s)$ in the cotnainer in all the three cases the partial pressure of I_2, i.e., pI_2 is assumed to be 1 atm in each case and is not considered in the problem so that

$$Q_p = \frac{[p\text{HI}(g)]^2}{pH_2(g)}$$

(*i*) pH_2 = 0.1 atm, pHI = 0.80 atm

$$Q_p = \frac{0.8\times0.8}{0.1} = \mathbf{6.4}$$

As the value of K_p is 0.35, this means that the equilibrium has not reached in the system. The reaction *has gone more towards the forward direction.*

(*ii*) pH_2 = 0.55 atm, pHI = 0.44 atm

$$Q_p = \frac{0.44\times0.44}{0.55} = \mathbf{0.352.}$$

As the value of concentration quotient (Q_p) is the same as that of the equilibrium constant (K_p),this means that the equilibrium has been reached in the reaction.

(*iii*) pH_2 = 2.5 atm, pHI = 0.15 atm

$$Q_p = \frac{0.15\times0.15}{2.5} = \mathbf{0.009.}$$

As the value of the concentration quotient (Q_p) is less than K_p, this means that equilibrium has not been reached in the reaction.

❑ Example 20.

Nitrogen and oxygen react to form nitrous oxide as :

$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$$

If a mixture of 0.482 mol N_2 and 0.933 mol O_2 is placed in a reaction vessel of 10.0 L and allowed to form N_2O at a temperature for which $K_c = 2.0\times10^{-37}$,what will be the composition of equilibrium mixture ?

N.C.E.R.T.

Solution: $2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$

$$K_c = \frac{[N_2O]^2}{[N_2]^2[O_2]}$$

Let us suppose that x mol of O_2 has reacted with $2x$ mol of N_2 to form $2x$ mol of N_2O. Then at equilibrium the concentrations are:

$N_2 = 0.482 - 2x$, $O_2 = 0.933 - x$ and $N_2O = 2x$

Since the volume of reaction vessel is 10.0 L, so the molar concentrations at equilibrium are:

$$[N_2] = \frac{0.482 - 2x}{10.0} = 0.0482 - 0.2x\text{ mol L}^{-1}$$

$$[O_2] = \frac{0.933 - x}{10.0} = 0.0933 - 0.1x\text{ mol L}^{-1}$$

$$[N_2O] = \frac{2x}{10.0} = 0.2x\text{ mol L}^{-1}$$

$$\therefore [K_c] = \frac{(0.2x)^2}{(0.0482 - 0.2x)^2\,(0.0933 - 0.1x)}$$

Since K_c is very small (2.0×10^{-37}), we can assume x to be very very small so that

$0.0482 - 0.2x \approx 0.0482$ and $0.0933 - 0.1x \approx 0.0933$

$$K_c = \frac{0.04x^2}{(0.0482)^2(0.0933)}$$

or $0.04x^2 = (0.0482)^2\,(0.0933)\times(2.0\times10^{-37})$

or $0.04x^2 = 4.34\times10^{-41}$

$$x^2 = \frac{4.34\times10^{-41}}{0.04} = 1.085\times10^{-39}$$

$$\therefore \quad x = 3.3\times10^{-20}$$

Thus, equilibrium concentrations are :

$[N_2] = 0.0482 - 0.2x = \mathbf{0.0482.}$

$[O_2] = 0.0933 - 0.1x = \mathbf{0.0933.}$

$[N_2O] = 0.2x = 0.2\times3.3\times10^{-20} = \mathbf{6.6\times10^{-21}.}$

❑ Example 21.

K_c for the reaction :

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

is 4.24 at 800 K. Calculate the equilibrium concentration of CO_2, H_2, CO and H_2O at 800 K, if only CO and H_2O are present initially at concentration of 0.10 M each ?

N.C.E.R.T.

Solution: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

Initial conc.	0.1	0.1	0	0
At equi	$0.1 - x$	$0.1 - x$	x	x

where x is the amount of CO_2 and H_2 formed at equilibrium

$$K_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]}$$

$$K_c = \frac{x\times x}{(0.1-x)\,(0.1-x)} = 4.24$$

$$x^2 = 4.24\,(0.01 + x^2 - 0.2\,x)$$

$$x^2 = 0.0424 + 4.24\,x^2 - 0.848x.$$

$$3.24x^2 - 0.848x + 0.0424 = 0$$

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Solving for x,

$$x = \frac{0.848 \pm \sqrt{(0.848)^2 - 4(3.24)(0.0424)}}{3.24 \times 2}$$

$x = 0.067$ and 0.194

[The value $x = 0.194$ should be neglected because it will give concentration of the reactant which is more than initial concentration]

Hence equilibrium concentrations are :

$$[CO_2] = [H_2] = 0.067 \text{ M}$$

$$[CO] = [H_2O] = 0.1 - 0.067 = \mathbf{0.033\ M.}$$

❑ Example 22.

At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass :

$$C(s) + CO_2(g) \rightleftharpoons 2CO\,(g)$$

Calculate K_c for this reaction at the above temperature.

N.C.E.R.T.

Solution: Let the total mass of the mixture of CO and CO_2 is 100g, then

CO = 90.55 *g* and $CO_2 = 100 - 90.55 = 9.45\ g$

$$\text{Moles of CO} = \frac{90.55}{28} = 3.234$$

$$\text{Moles of } CO_2 = \frac{9.45}{44} = 0.215$$

$$\text{Mole of fraction of CO} = \frac{3.234}{3.234 + 0.215} = 0.938$$

$$\text{Mole fraction of } CO_2 = 1 - 0.938 = 0.062$$

$\therefore$ p_{CO} = mole of fraction × total pressure

$= 0.938 \times 1$ atm $= 0.938$ atm

$p_{CO_2} = 0.062 \times 1$ atm $= 0.062$ atm

K_p for the reaction

$$C(s) + CO_2\,(g) \rightleftharpoons 2CO(g)$$

$$K_p = \frac{(p_{CO})^2}{(p_{CO_2})} = \frac{(0.938)^2}{0.062} = 14.19$$

Now $\Delta n_g = 2 - 1 = 1$

$K_p = K_c\,(RT)^{\Delta n_g}$

or $K_c = \dfrac{K_p}{RT} = \dfrac{14.19}{0.0821 \times 1127} = \mathbf{0.153.}$

❑ Example 23.

Two moles of PCl_5 were introduced in a 2L flask and heated at 600 K to attain the equilibrium. PCl_5 was found to be 40% dissociated into PCl_3 and Cl_2. Calculate the value of K_c.

Solution: PCl_5 dissociates as :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial concentration of PCl_5 = 2 mol

%age dissociation at equilibrium = 40%

$\therefore$ Number of moles of PCl_5 dissociated $= \dfrac{2 \times 40}{100} = 0.8$ mol

Now, 1 mol of PCl_5 on dissociation gives 1 mole of PCl_3 and 1 mole of Cl_2, therefore, concentration at equilibrium

$PCl_5 = 2.0 - 0.8 = 1.2$ mol, $PCl_3 = 0.8$ mol, $Cl_2 = 0.8$ mol.

Since volume of flask is 2L, molar concentrations are :

$$[PCl_5] = \frac{1.2}{2} = 0.6 \text{ mol L}^{-1},\ [PCl_3] = \frac{0.8}{2} = 0.4 \text{ mol L}^{-1}$$

$$[Cl_2] = \frac{0.8}{2} = 0.4 \text{ mol L}^{-1}$$

Now, $K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]} = \dfrac{(0.4) \times (0.4)}{(0.6)} = \mathbf{0.267\ mol\ L^{-1}}$

❑ Example 24.

(a) In an experiment at 1000 K, the concentrations of different species are :

$[NH_3] = 0.105$ mol dm^{-3}, $[N_2] = 1.10$ mol dm^{-3} and $[H_2] = 1.50$ mol dm^{-3}

Calculate the values of K_c and K_p for the reaction :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

(b) What will be the K_c for the reaction :

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

Solution: (*a*) For the reaction,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$[NH_3] = 0.105$ mol dm^{-3}, $[N_2] = 1.10$ mol dm^{-3} and $[H_2] = 1.50$ mol dm^{-3}

$$K_c = \frac{(0.105 \text{ mol dm}^{-3})^2}{(1.10 \text{ mol dm}^{-3}) \times (1.50 \text{ mol dm}^{-3})^3}$$

$= 2.97 \times 10^{-3}$ mol^{-2} dm^6

Now, $K_p = K_c\,(RT)^{\Delta n}$

$\Delta n = 2 - (3 + 1) = -2$,

R = 0.082 atm dm^3 K^{-1} mol^{-1}, T = 1000 K

$\therefore$ $K_p = (2.97 \times 10^{-3}$ mol^{-2} dm$^6) \times [(0.082$ atm dm^3 K^{-1} mol$^{-1}) \times (1000$ K$)]^{-2}$

$= \mathbf{4.42 \times 10^{-7}\ atm^{-2}.}$

(*b*) The equilibrium constant K_c for the reverse reaction is related to the equilibrium constant K_c for the forward reaction as :

$$K'_c = \frac{1}{K_c} = \frac{1}{2.97 \times 10^{-3} \text{ mol}^{-2} \text{ dm}^6}$$

$= \mathbf{3.37 \times 10^{-2}\ mol^2\ dm^{-6}.}$

❑ Example 25.

The equilibrium constant for the reaction,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is 16 at 600 K. What will be the concentration of H_2, I_2 and HI if two moles of hydrogen and three moles of iodine are injected into a litre flask.

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Solution: Let us suppose that x moles/litre of hydrogen react. This will react with x moles of iodine and form $2x$ moles of HI. Then the concentrations at equilibrium are :

$$[H_2] = 2-x,\ [I_2] = 3-x, \qquad [HI] = 2x$$

Now, $K = \dfrac{[HI]^2}{[H_2][I_2]}$

$\therefore \quad 16 = \dfrac{(2x)^2}{(2-x)(3-x)}$

$16(2-x)(3-x) = 4x^2$

or $4(2-x)(3-x) = x^2$

or $4(6-5x+x^2) = x^2$

or $24 - 20x + 4x^2 = x^2$

or $3x^2 - 20x + 24 = 0$

By solving the above quadratic equation for x, we get

$$x = \frac{20 \pm \sqrt{400 - 4\times 3\times 24}}{2\times 3}$$

$x = 1.56$ or 5.1

Here $x = 1.56$ as its value cannot exceed 5 because initial number of moles of H_2 and I_2 are less than 5. Thus equilibrium concentrations are :

$[H_2] = 2.0 - 1.56 = 0.44$ mol L^{-1}

$[I_2] = 3.0 - 1.56 = 1.44$ mol L^{-1}

$[HI] = 2 \times 1.56 = 3.12$ mol L^{-1}

❑ Example 26.

13.8 g of N_2O_4 was placed in a 1L reaction vessel at 400 K and allowed to attain equilibrium :

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

The total pressure at equilibrium was found to be 9.15 bar. Calculate K_c, K_p and partial pressure at equilibrium. **N.C.E.R.T.**

Solution: We know that

$$pV = nRT$$

Moles of $N_2O_4 = \dfrac{13.8}{92} = 0.15$ (Molar mass of $N_2O_4 = 92$)

$R = 0.083$ bar L mol^{-1} K, $T = 400$K, $V = 1$L

$\therefore \quad p = \dfrac{nRT}{V} = \dfrac{0.15\times 0.083\times 400}{1} = 4.98$ bar

	$N_2O_4 \rightleftharpoons$	$2NO_2$
Initial conc.	4.98	0
At equi.	4.98–x	$2x$.

Total pressure = $4.98 - x + 2x = 9.15$ bar

$x = 9.15 - 4.98 = 4.17$ bar

$p_{N_2O_4} = 4.98 - 4.17 = 0.81$ bar

$p_{NO_2} = 4.17 \times 2 = 8.34$ bar

$$K_p = \frac{(p_{NO_2})^2}{(p_{N_2O_4})} = \frac{(8.34)^2}{0.81} = 85.87$$

Now, $K_c = K_p \left(\dfrac{1}{RT}\right)^{\Delta n_g}$

$\Delta n_g = 2 - 1 = 1$

$$K_c = 85.87 \times \frac{1}{(0.083\times 400)^1}$$

$= \mathbf{2.586 = 2.6}$

❑ Example 27.

The degree of dissociation of PCl_5 at a certain temperature and under atmospheric pressure is 0.2. Calculate the pressure at which it will be half dissociated at the same temperature.

Solution: PCl_5 dissociates as :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

If α is the degree of dissociation at certain temperature under atmospheric pressure, then

	$PCl_5 \rightleftharpoons$	PCl_3	+ Cl_2
Initial conc.	1	0	0
At equi.	$1-\alpha$	α	α

Total number of moles at equilibrium $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

Partial pressures of PCl_5, PCl_3 and Cl_2 will be

$$p(PCl_5) = \frac{1-\alpha}{1+\alpha}.P \qquad p_{(PCl_3)} = \frac{\alpha}{1+\alpha}.P$$

$$p(Cl_2) = \frac{\alpha}{1+\alpha}.P$$

Now, $K_p = \dfrac{p(PCl_3).\,p(Cl_2)}{p(PCl_5)}$

$$= \frac{\left(\frac{\alpha}{1+\alpha}.P\right)\times\left(\frac{\alpha}{1+\alpha}.P\right)}{\frac{1-\alpha}{1+\alpha}.P} = \frac{\alpha^2}{1-\alpha^2}P$$

Putting P = 1 atm and $\alpha = 0.2$

$$K_p = \frac{(0.2)^2}{1-(0.2)^2}\times 1 = 0.041$$

When $\alpha = \dfrac{1}{2} = 0.5$, let pressure is P′

$$K_p = \frac{\alpha^2}{1-\alpha^2}.P'$$

$$0.041 = \frac{(0.5)^2 P'}{1-(0.5)^2}$$

$$P' = \frac{(0.041)\,[1-(0.5)^2]}{(0.5)^2} = \mathbf{0.125\ atm}$$

❑ Example 28.

Nitric oxide reacts with bromine and gives nitrosyl bromide according to the reaction :

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

When 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at constant temperature 0.0518 mol of NOBr is obtained at equilibrium. Calculate (i) the equilibrium amount of nitric oxide and bromine (ii) equilibrium constant. **N.C.E.R.T.**

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Solution: $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$

(*i*) According to the above equation

0.0518 mol of NOBr are formed from 0.0518 mol of NO

∴ Amount of nitric oxide at equilibrium

$= 0.087 - 0.0518$

$= 0.0352$ mol

Similarly, 0.0518 mol of NOBr are formed from $\frac{0.0518}{2}$ mol of Br_2

∴ Amount of bromine at equilibrium

$= 0.0437 - \frac{0.0518}{2} = 0.0178$ mol

(*ii*) $K_c = \frac{[NOBr]^2}{[NO]^2\,[Br_2]}$

At equilibrium, [NOBr] = 0.0518 mol,

[NO] = 0.0352 mol

$[Br_2]$ = 0.0178 mol

∴ $K_c = \frac{(0.0518)^2}{(0.0352)^2 \times (0.0178)} = \mathbf{121.66.}$

❑ Example 29.

A sample of HI(g) is placed in a flask at a pressure of 0.2 atm. At equilibrium partial pressure of HI (g) is 0.04 atm. What is K_p for the given equilibrium reaction :

$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ **N.C.E.R.T.**

Solution: Initial pressure of HI = 0.2 atm

Partial pressure of HI at equilibrium = 0.04 atm

Decrease in pressure after dissociation = 0.2 – 0.04 = 0.16 atm

Partial pressure of H_2 after dissociation = $\frac{0.16}{2}$ atm = 0.08 atm

∴ Partial presssure of I_2 after dissociation = 0.08 atm

Then	$2HI(g) \rightleftharpoons$	$H_2(g)$	+ $I_2(g)$
Initial pressure	0.2 atm	0	0
Pressure at equi.	0.04	0.08	0.08

$K_p = \frac{p_{H_2} \times p_{I_2}}{p_{HI}^2} = \frac{0.08 \times 0.08}{(0.04)^2} = \mathbf{4.0}$

❑ Example 30.

The value of K_p for the reaction,

$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

is 3.0 bar at 1000 K. If initially $p_{CO_2} = 0.48$ bar and $p_{CO} = 0$ bar and pure graphite is present, calculate the equilibrium partial pressure of CO and CO_2.

N.C.E.R.T.

Solution: Let x be the amount of CO_2 reacted,

	$CO_2(g)$ + $C(s)$ $\rightleftharpoons$	$2CO(g)$
Init. press.	0.48 bar	0
At equ	(0.48–x) bar	2 x bar

$K_p = \frac{(p_{CO})^2}{p_{CO_2}} = \frac{(2x)^2}{(0.48-x)}$

or $3 = \frac{4x^2}{0.48-x}$

or $4x^2 = 3(0.48 - x)$

$4x^2 = 1.44 - 3x$

or $4x^2 + 3x - 1.44 = 0$

Solving for x,

$x = \frac{-3 \pm \sqrt{3^2 - 4\times4\times(-1.44)}}{2\times4}$

$= \frac{-3 \pm 5.66}{8}$

$x = \frac{2.66}{8} = 0.33$

(negative value of x is neglected because x cannot be negative)

The equilibrium pressures are

$p_{CO} = 2x = 2 \times 0.33 = 0.66$ bar

$p_{CO_2} = 0.48 - x = 0.48 - 0.33 = 0.15$ bar

Practice Problems

16. If 1 mole of acetic acid and 1 mole of ethyl alcohol are mixed together and the reaction proceeds to the equilibrium, the concentration of acetic acid and water are found to be 1/3 and 2/3 mole respectively. Calculate the equilibrium constant.

17. Two moles of HI when heated at 444°C until equilibrium is reached were found to be 22% dissociated. Calculate equilibrium constant for the reaction.

18. One mole each of hydrogen and iodine are allowed to react at certain temperature till the equilibrium is reached. Calculate the composition of equilibrium mixture if K = 66.5.

19. Equilibrium constant K_c for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500 K is 0.061. At a particular time, the analysis shows that composition of the reaction mixture is 3.00 mol L^{-1} N_2, 2.00 mol L^{-1} H_2 and 0.500 mol L^{-1} NH_3. Is the reaction at equilibrium ? If not, in which direction does the reaction tend to proceed to reach equilibrium?

20. For the reaction :

$CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$ at 1173 K, $K_c = 3.6$. For each of the following compositions predict whether the reaction mixture is at equilibrium or not. If it is not, decide to which direction, the reaction should go :

(*i*) $[CH_4] = 1.07$ M, $[H_2S] = 1.20$ M, $[CS_2]$ 0.90 M, $[H_2] = 1.78$ M

(*ii*) $[CH_4] = 1.45$ M, $[H_2S] = 1.29$ M, $[CS_2] = 1.25$ M, $[H_2] = 1.75$ M

21. At a certain temperature, equilibrium constant (K_c) is 16 for the reaction.

$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

If we take one mole each of all the four gases in a 1 L container, what would be the equilibrium concentrations of NO and NO_2 ?

22. 1.5 moles of PCl_5 are heated at a constant temperature in a closed vessel of 4 L capacity. At the equilibrium, PCl_5 is found to be 35% dissociated into PCl_3 and Cl_2. Calculate the equilibrium constant.

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23. For the reaction at 127°C

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

the partial pressures of N_2 and H_2 are 0.80 and 0.40 atm respectively at equilibrium. The total pressure of the system is 2.80 atm. Calculate K_p and K_c for the reaction.

24. The equilibrium constant, K_p for a reaction is 900 atm^{-1} at 800 K.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

A mixture containing SO_3 and O_2 having initial partial pressures of 1 and 2 atm respectively is heated at a constant volume to equilibriate. Calculate the partial pressure of each gas at 800 K.

25. A vessel at 1000 K contains carbon dioxide with a pressure of 0.5 atm. Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of K if the total pressure at equilibrium is 0.8 atm.

26. At 25°C and one atmospheric pressure, the partial pressures in equilibrium mixture of N_2O_4 and NO_2 are 0.7 and 0.3 atmosphere respectively. Calculate the partial pressure of these gases when they are in equilibrium at 25°C and at a total pressure of 10 atmospheres.

27. At 207°C, for the reaction :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

it is found that at equilibrium, the mixture contains 52% of ammonia. If the pressure of the mixture is 10 atm, calculate K_p and K_c for the reaction.

28. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained concentration of PCl_5 was found to be 0.05 mol L^{-1}. If value of K_c is 8.3×10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium ?

29. Some solid NH_4HS is placed in a flask containing 0.5 atm NH_3. What would be the pressure of NH_3 and H_2S when equilibrium is reached ?

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g), \quad K_p = 0.11$$

30. When sulphur in the form of S_8 is heated at 900 K, the initial pressure of 1 atm falls by 29% at equilibrium. This is because of conversion of S_8 to S_2. Calculate the equilibrium constant for the reaction. *(Roorkee 1990)*

31. A gaseous compound XY_2 dissociates as:

$$XY_2(g) \rightleftharpoons XY(g) + Y(g)$$

If the initial pressure is 500 mm of Hg and the total pressure at equilibrium is 700 mm of Hg, calculate K_p for the reaction. ***N.C.E.R.T.***

32. Phosphorus pentachloride decomposes according to the reaction :

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

1.50 mol of PCl_5 is placed in a 500 mL of closed reaction vessel and allowed to reach equilibrium with its decomposition products, phosphorus trichloride and chlorine at 523 K. Equilibrium constant K_c is 1.80. What is the composition of mixture at equilibiurm ? ***N.C.E.R.T.***

33. For the following reaction equilibrium

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$$

$K_c = 6.3 \times 10^{14}$ at 1000 K. Both the forward and reverse reaction in the equilibrium are elementary bimolecular reactions. What is K_c for the reverse reaction ? ***N.C.E.R.T.***

34. A mixture of 1.571 mol of N_2, 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced nito a 20L reaction vessel at 500 K. At this temperature the equilibrium constant, K_c for the reaction,

$N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g)$ is 1.7×10^2.

Is the reaction mixture at equilibrium ? If not what is the direction of the net reaction ? ***N.C.E.R.T.***

35. The value of K_c for the reaction;

$$2A \rightleftharpoons B + C \text{ is } 2 \times 10^{-3}$$

At a given time,the concentration of reaction mixture is $[A] = [B] = [C] = 3 \times 10^{-4}$ M. In which direction will the reaction proceed ? ***N.C.E.R.T.***

36. 3.0 mol of PCl_5 kept in 1L reaction vessel was allowed to attain equilibrium at 380 K. Calculate the composition of the mixture at equilibrium if $K_c = 1.80$. ***N.C.E.R.T.***

37. At 700 K, equilibrium constant for the reaction :

$$H_2(g) = I_2(g) \rightleftharpoons 2HI(g)$$

is 54.8. If 0.5 mol L^{-1} of $HI(g)$ is present at equilibrium at 700 K, what are the concentrations of $H_2(g)$ and $I_2(g)$ assuming that initially we started with $HI(g)$ and allowed it to reach equilibrium at 700 K. ***N.C.E.R.T.***

38. $K_p = 0.44$ atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium ?

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

N.C.E.R.T.

Answers to Practice Problems

16. 4.0 **17.** 0.0199
18. $[H_2] = 0.197$, $[I_2] = 0.197$,(HI) = 1.606
19. Q = 0.0104, reaction will proceed to form more products
20. (*i*) backward direction
(*ii*) backward direction
21. [NO] = 1.6 mol, $[NO_2]$ = 0.4 mol.
22. 0.071
23. 50 atm^{-2}, 53.8×10^3 mol^{-2} L^2
24. $p_{SO_2} = 0.0236$, $p_{O_2} = 2.0118$, $p_{SO_3} = 0.976$
25. 1.8 atm.

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26. $p_{N_2O_4}$ = 8.92 atm, p_{NO_2} = 1.08 atm.
27. 0.4830, 750.1 **28.** 0.024 mol L^{-1}
29. 0.665 atm, 0.1653 atm. **30.** 2.55 atm^3
31. 133.3
32. (PCl_3) = 1.59 mol L^{-1}, (Cl_2) = 1.59mol L^{-1}, (PCl_5) = 1.41 mol L^{-1}.
33. 1.587×10^{-15}
34. $Q = 2.38 \times 10^3$, No reaction is not at equilibrium.
35. in reverse direction **36.** 1.413, 1.59, 1.59 M
37. $[H_2] = [I_2] = 0.068$ M **38.** 3.62 atm

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RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT K, REACTION QUOTIENT Q AND GIBBS FREE ENERGY

We have learnt in unit 6, that the value of equilibrium constant is directly related to the thermodynamics of the reaction and in particular to the change in Gibbs energy, ΔG. The change in Gibbs energy is related to composition of reaction mixture as

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where ΔG° is standard Gibbs energy change. At equilibrium, when $\Delta G = 0$ and $Q = K_c$, the above equation becomes

$$0 = \Delta G^\circ + RT \ln K_c$$

or $$\Delta G^\circ = -RT \ln K_c$$

or $$\mathbf{\Delta G^\circ = -2.303\ RT \log K_c}$$

The above equation may also be written as :

$$\ln K_c = -\Delta G^\circ/RT$$

Taking antilog of both the sides we get

$$K_c = e^{-\Delta G^\circ/RT}$$

The equation is very important in chemical thermodynamics because it gives relation between equilibrium constant for any process (physical or chemical) and standard Gibbs energy change. It can help to predict spontaneity in terms of the value of ΔG°. We can also conclude :

- If $\Delta G^\circ < 0$, then $-\Delta G^\circ/RT$ is positive and $e^{-\Delta G^\circ/RT}$ becomes greater than 1, making $K > 1$. This implies a spontaneous reaction or the reaction which proceeds in the forward direction to such an extent that the products are present predominantly.
- If $\Delta G^\circ > 0$, then $-\Delta G^\circ/RT$ is negative and $e^{-\Delta G^\circ/RT}$ becomes less than 1 and $K < 1$. This implies a non spontaneous reaction or a reaction which proceeds in the forward direction to such a small extent that only a very small quantity of products are formed. Thus,

$K < 1$ when $\Delta_r G^\circ > 0$
$K > 1$ when $\Delta_r G^\circ < 0$

SOLVED EXAMPLES

Example 31.

For the water gas reaction :

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2O(g)$$

the standard Gibbs energy for the reaction at 1000 is –8.1 kJ mol^{-1}. Calculate its equilibrium constant.

Solution: We know

$$\Delta G^\circ = -2.303\ RT \log K$$

or $$\log K = \frac{-\Delta G^\circ}{2.303RT}$$

$\Delta G^\circ = -8.1$ kJ mol^{-1}, T = 1000 ,

$R = 8.314 \times 10^{-3}$ kJ mol^{-1} K^{-1}

$$\therefore \quad \log K = -\frac{-8.1}{2.303 \times 8.314 \times 10^{-3} \times 1000}$$

$$= 0.423$$

or $$K = \mathbf{2.64.}$$

Example 32.

Calculate ΔG° for conversion of oxygen to ozone :

$$\frac{3}{2} O_2(g) \longrightarrow O_3(g) \text{ at } 298\ K.$$ **N.C.E.R.T.**

K_p for this conversion is 2.47×10^{-29}.

Solution: We know

$$\Delta G^\circ = -2.303\ RT \log K$$

$R = 8.314$ J mol^{-1} K^{-1}, T = 298 K, $K = 2.47 \times 10^{-29}$

$$\therefore \quad \Delta G^\circ = -2.303 \times (8.314\ J\ mol^{-1}\ K^{-1}) \times (298\ K) \times \log (2.47 \times 10^{-29})$$

$$= \mathbf{163.2\ kJ\ mol^{-1}.}$$

Example 33.

Hydrolysis of sugar gives :

$$Sucrose + H_2O \rightleftharpoons Glucose + Fructose$$

Equilibrium constant K_c for the reaction is 2×10^{13} at 300 K. Calculate ΔG° at 300 K

Solution: $\Delta G^\circ = -2.303\ RT \log K$

$K = 2 \times 10^{13}$, T = 300K, R = 8.314 J mol^{-1} K^{-1}.

$$\therefore \quad \Delta G^\circ = -2.303 \times (8.314\ J\ mol^{-1}\ K^{-1}) \times (300\ K) \times \log 2 \times 10^{13}$$

$$= -7.64 \times 10^4\ J\ mol^{-1}$$

$$= \mathbf{-76.4\ kJ\ mol^{-1}.}$$

Example 34.

The value of ΔG° for the phosphorylation of glucose in glycolysis is 13.8 kJ mol^{-1}. Find the value of K_c at 298 K. **N.C.E.R.T.**

Solution: $\Delta G^\circ = 13.8$ kJ $mol^{-1} = 13.8 \times 10^3$ Jmol^{-1}

$$\Delta G^\circ = -2.303\ RT \log K$$

or $$\log K = -\frac{\Delta G^\circ}{2.303\ RT}$$

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$$= -\frac{13.8\times10^{3}}{2.303\times8.314\times298}$$

$$= -2.418$$

$$K = \mathbf{3.82\times10^{-3}}$$

❑ **Example 35.**

Calculate (a) ΔG° and (b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K

$$NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$$

Where $\Delta_f G^\circ(NO_2) = 52.0\ kJ\ mol^{-1}$,

$\Delta_f G^\circ(NO) = 87.0\ kJ\ mol^{-1}$

$\Delta_f G^\circ(O_2) = 0\ kJ\ mol^{-1}$ **N.C.E.R.T.**

Solution: $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$

$$\Delta G^\circ = \Delta_f G^\circ(NO_2) - [\Delta_f G^\circ(NO) + \frac{1}{2}\Delta_f G^\circ(O_2)]$$

$$= 52.0 - 87.0 - \frac{1}{2}\times0 = -35\ kJ\ mol^{-1}$$

Now $\log K = -\frac{\Delta G^\circ}{2.303RT}$

$$= -\frac{-35\times10^{3}\ J\ mol^{-1}}{2.303\times8.314\ JK^{-1}\ mol^{-1}\times298\ K}$$

$$= 6.314$$

or $K = \mathbf{1.362\times10^{6}}$.

Practice Problems

39. The standard Gibbs energy change for the reaction

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

is –142 kJ mol^{-1} at 300 K. Calculate equilibrium constant.

40. Calculate ΔG° for the reaction

$$NO \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$$

if $K = 1.55\times10^{15}$ at 298 K.

41. For the equilibrium reaction

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l) \text{ at } 298\ K$$

$\Delta G^\circ = -474.78$ kJ mol^{-1}. Calculate log K for it.

(D.S.B. 2001)

42. The equilibrium constant for the reaction :

$$Co^{3+}(aq) + 6NH_3(aq) \rightleftharpoons [Co(NH_3)_6]^{3+}(aq)$$

is 2.0×10^{-7}. Calculate the value of ΔG° at 25°C

Answers to Practice Problems

39. 5.25×10^{24} **40.** –86.7 kJ mol^{-1}

41. 83.21 at 25°C **42.** –12.023 kJ.

Hints & Solutions on page 94

FACTORS AFFECTING THE STATE OF EQUILIBRIUM : LE-CHATELIER'S PRINCIPLE

Le-Chatelier and Braun (1884), French chemists, made certain generalizations to explain the effect of changes in concentration, temperature or pressure on the state of system in equilibrium. When a system is subjected to a change in one of these factors, the equilibrium gets disturbed and the system readjusts itself until it returns to equilibrium. The generalization is known as **Le-Chatelier's principle.** It may be stated as :

If a system in equilibrium is subjected to a change in any of the factors that determine the equilibrium conditions of a system then the equilibrium will shift in the direction so as to reduce or to counteract the effect of the change.

The principle is very helpful in predicting *qualitatively* the effect of change in concentration, pressure or temperature on a system in equilibrium. This is applicable to all physical and chemical equilibria. Let us now apply Le-Chatelier's principle to explain the effect of changes in concentrations, temperature and pressure on various reactions in equilibrium.

1. Effect of Change of Concentration

When the equilibrium is disturbed by the addition or removal of any reactant or product, then the equilibrium shifts in the direction to counteract the effect of change in concentration of reactant or product. In other words,

- When a substance (reactant or product) is added to an equilibrium mixture, the stress is relieved by the net reaction in the direction that **consumes the added substance.**
- When a substance (reactant or product) is removed from an equilibrium mixture, then the stress is relieved by the net reaction in the direction that **replenishes** the removed substance.

To understand this, consider the reaction :

$$H_2(g) + I_2(g) \rightleftharpoons 2HI$$

Suppose at equilibrium, a little amount of H_2 is added to the system, so that the concentration of H_2 is increased and it is no longer its equilibrium concentration. According to Le-Chatelier's principle, the equilibrium will shift in the direction in which the concentration of H_2 is decreased. As a result, a new equilibrium will be set up in which the concentration of H_2 should be less than it was after the addition of H_2 but more than what it was in the original mixture. *It may be noted that adjustment of equilibrium never fully compensates for the change in concentration that*

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was made. Here, equilibrium will shift in the direction, which can consume H_2. This is only possible if more of H_2 is used up in combination with I_2 to form more HI. Thus, equilibrium will shift in the forward direction as shown in Fig. 14.

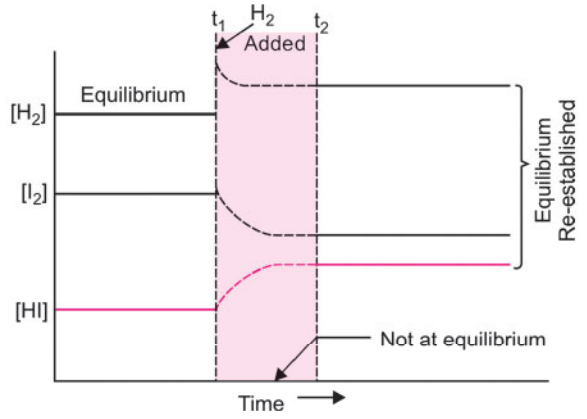

Fig. 14. Effect of addition of H_2 on change of concentration for the reactants and products in the reaction.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The same conclusion can be derived by considering the reaction quotient , Q_c.

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} \quad \text{At equilibrium, } Q_c = K$$

If H_2 is added at equilibrium, H_2 increases and Q_c becomes less than K. As a result, the reaction moves in the forward direction *i.e.,* H_2 and I_2 decrease and HI increases until Q_c = K. Similarly, if the concentration of HI (product) is increased at equilibrium, the system will move in the backward direction so as to decrease the concentration of HI. In general, it may be concluded that

- ***If concentration of one or all the reactant species is increased, the equilibrium shifts in the forward direction and more of the products are formed.***
- ***If the concentration of one or all the product species is increased, the equilibrium shifts in the backward direction forming more reactants.***

It may be noted that the removal of a product from the reaction mixture often has a great importance in industrial processes. By removing one of the products from the reaction mixture, it keeps the reaction in the forward direction and prevents the reaction to come to equilibrium without going to completion. Generally, a gaseous substance that can be easily vapourized is removed. For example, during the manufacture of ammonia, the ammonia is liquefied and removed from the reaction mixture so that reaction moves in the forward direction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Similarly, during the large scale production of lime, CaO, from $CaCO_3$ as :

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

CO_2 is constantly removed from the kiln to get maximum yield of CaO. It should be remembered that continuous removal of a product, maintains Q_c less than K_c and the reaction continues to move in the forward direction.

Effect of concentration : An illustrative experiment

The effect of concentration on equilibrium can be easily **demonstrated** by the following experiment :

$$\underset{\text{Pale yellow}}{Fe^{3+}(aq)} + \underset{\text{Colourless}}{SCN^-(aq)} \rightleftharpoons \underset{\text{Reddish brown}}{[FeSCN]^{2+}(aq)}$$

$$K_c = \frac{[Fe(SCN)(aq)]^{2+}}{[Fe^{3+}(aq)][SCN^-(aq)]}$$

A reddish brown colour appears on adding two drops of 0.002 M potassium thiocyanate solution to 10 ml of 0.2 M iron (III) nitrate solution due to the formation of $[Fe(SCN)]^{2+}$. After sometime, the intensity of red colour becomes constant on attaining equilibrium. This equilibrium can be shifted in either forward or backward direction depending on our choice of adding of a reactant or a product.

Suppose some potassium thiocyanate, capable of giving SCN^- ions is added to the above equilibrium. The colour of the solution darkens immediately showing thereby the formation of $[Fe(SCN)]^{2+}$ ion. In other words, the equilibrium shifts towards forward direction. Similarly, if the concentration of Fe^{3+} ions is increased by adding some ferric salt (say $FeCl_3$), colour deepens again due to the formation of more of $[FeSCN]^{2+}$ ions. Thus, the increase in concentration of either Fe^{3+} or SCN^- ions (reactants) pushes the system in the forward direction (deep colour) so as to undo the effect of the increase in the concentration of Fe^{3+} or SCN^- ions. This is exactly in accordance with Le-Chatelier's principle.

Now, suppose the concentration of $[FeSCN]^{2+}$ ions is increased at the equilibrium by adding a small amount of potassium ferrosulphocyanide capable of giving complex ions. Then, it is observed that the colour of the solution becomes less dark showing that the dark coloured $[FeSCN]^{2+}$ ions have changed to Fe^{3+} and SCN^- ions. In other words, the equilibrium shifts towards reactants.

The shift in equlibrium can also be understood by removing the reactants or products. For example, oxalic acid ($H_2C_2O_4$) reacts with Fe^{3+} ion to form stable complex ion $Fe(C_2O_4)_3^{3-}$, thereby decreasing the concentration of free Fe^{3+} ions. So, if

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some oxalic acid is added, the concentration of Fe^{3+} ions decreases and the equilibrium is shifted in backward direction by dissociation of $[Fe(SCN)]^{2+}$ ions. Because of the decrease of concentration of $[Fe(SCN]^{2+}$ ion, red colour decreases.

Addition of $HgCl_2$ also decreases red colour because Hg^{2+} ions react with SCN^- ions to form stable $[Hg(SCN)_4]^{2-}$ ions. Removal of free SCN^- ions shifts the equilibrium from right to left to replenish SCN^-.

Thus, it may be concluded that :

Increase in concentration of any of the reactants $\xrightarrow{\text{Shifts the equilibrium to}}$ **Forward direction**

Increase in concentration of any of the products $\xrightarrow{\text{Shifts the equilibrium to}}$ **Backward direction**

In case of systems involving gaseous substances, the concentrations are taken as partial pressures of the substances.

The effect of change in concentration on equilibrium may be applied to many phenomena occurring in our body. For example :

***(i)* Carriage of oxygen by haemoglobin in blood.** The haemoglobin (Hb) in red corpuscles of our blood carries oxygen to the tissues. This involves the equilibrium,

$$Hb(s) + O_2(g) \rightleftharpoons HbO_2(s)$$

The blood that is in equilibrium with the oxygen of the air in the lungs finds a situation in the tissues where the partial pressure of oxygen is low. According to Le-Chatelier's principle, the equilibrium shifts towards the left so that some of the oxyhaemoglobin changes to haemoglobin giving up the oxygen. When the blood returns to the lungs, the partial pressure of the oxygen is higher and the equilibrium favours the formation of more oxyhaemoglobin.

***(ii)* Removal of carbon dioxide from the tissues by blood.** Blood removes CO_2 from the tissues. The equilibrium is

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Carbon dioxide dissolves in the blood in the tissues since the partial pressure of CO_2 is high. However in the lungs, where the partial pressure of CO_2 is low, it is released from the blood.

***(iii)* Sweet substances cause tooth decay.** Tooth enamel consists of an insoluble substance called hydroxyapatite, $Ca_5(PO_4)_3OH$. The dissolution of this substance from the teeth is called *demineralization* and its formation is called *remineralization*. Even with the healthy teeth, there is an equilibrium in the mouth as

$$Ca_5(PO_4)_3OH(s) \underset{\text{endothermic}}{\overset{\text{exothermic}}{\rightleftharpoons}} 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$$

When sugar substances are taken, sugar is absorbed on teeth and gets fermented to give H^+ ions. The H^+ ions produced disturb the equilibrium by combining with OH^- to form water and with PO_4^{3-} to form HPO_4^{2-}. Removal of products cause the equilibrium to shift towards right and therefore, $Ca_5(PO_4)_3OH$ dissolves causing tooth decay.

2. Effect of Change of Temperature

According to Le-Chatelier's principle, if the temperature of the system at equilibrium is increased (heat is supplied), the equilibrium will shift in the direction in which the added heat is absorbed. In other words, *the equilibrium will shift in the direction of* **endothermic reaction** *with increase in temperature. Alternatively, the decrease in temperature will shift the equilibrium towards the direction in which heat is produced and, therefore, will favour* **exothermic reaction.**

Thus, is general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction :

- The equilibrium constant for an **exothermic reaction** (negative ΔH) decreases as temperature increases.
- The equilibrium constant for an **endothermic reaction** (positive ΔH) **increases as temperature *increases*.**

We have studied that in every system, at equilibrium an endothermic and exothermic reaction take place simultaneously. If the forward reaction is exothermic, backward reaction will be endothermic or *vice versa*. For example, consider the equilibrium for an **exothermic reaction,**

$$N_2(g) + 3H_2(g) \underset{\text{endothermic}}{\overset{\text{exothermic}}{\rightleftharpoons}} 2NH_3(g); \quad \Delta_r H^\circ = -92.38 \text{ kJ}$$

In this equilibrium, the forward reaction is exothermic while the backward reaction is endothermic. Now, if the temperature is increased, the equilibrium will change in the direction of endothermic reaction, which tends to undo the effect of added heat. Since the backward reaction is endothermic, so this reaction will be favoured by increasing temperature. In other words, increase in temperature will result into lesser amount of ammonia. On the other hand, if temperature is decreased, the equilibrium will shift towards exothermic reaction *i.e.,* forward direction in the formation of ammonia.

In the case of reaction between nitrogen and oxygen, the forward reaction is endothermic while the backward reaction is exothermic. According to Le-Chatelier's principle, the increase in temperature will

$$N_2(g) + O_2(g) \underset{\text{exothermic}}{\overset{\text{endothermic}}{\rightleftharpoons}} 2NO(g); \quad \Delta_r H^\circ = +180 \text{ kJ}$$

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favour the forward (endothermic) reaction. This is because the equilibrium shifts towards the direction in which heat is absorbed to relieve the system of the stress of added heat. On the other hand, decrease in temperature shifts the equilibrium in the direction of exothermic reaction, *i.e,* in favour of reactants in the above example.

Let us apply the Le-Chatelier principle to the solubility of certain substances. For example, when NH_4Cl and $NaNO_3$ are dissolved in water, heat is absorbed,

$$NH_4Cl(s) + aq + \text{heat} \rightleftharpoons NH_4Cl(aq)$$

while in case of $CaCl_2$ heat is evolved,

$$CaCl_2 + aq \rightleftharpoons CaCl_2\,(aq) + \text{heat}$$

Obviously, **the solubility of NH_4Cl and $NaNO_3$ will increase while that of $CaCl_2$ will decrease with increase of temperature.**

Effect of Temperature : An illustrative experiment :

The effect of temperature on equilibrium can be easily demonstrated by performing the dimerization reaction of NO_2 gas to N_2O_4.

$$2NO_2\,(g) \rightleftharpoons N_2O_4\,(g);\quad \Delta_r H = -57.2 \text{ kJ mol}^{-1}$$

Prepare NO_2 gas by adding copper turnings to conc. HNO_3 and collect the gas through a delivery tube in two test tubes each of 5 mL. Check equal intensity of the colour of the gas in each test tube and seal the stopper of the tube with araldite. Now take three 250 mL beakers and label them as 1, 2 and 3. Fill beaker 1 with freezing mixture, beaker 2 with water at room temperature and beaker 3 with hot water (about 363 K temperature). When both the test tubes are placed in beaker 2, intensity of brown colour of the gas is almost equal. After keeping the test tubes for about 10 – 15 minutes in water maintained at room temperature, remove them and place one test tube in

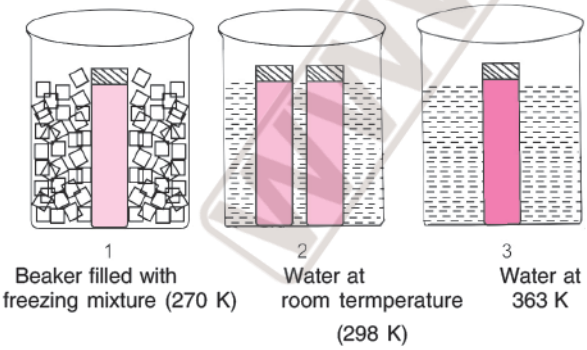

Fig. 15. Effect of temperature an equilibrium for the reaction : $2NO_2(g) \rightleftharpoons N_2O_4(g)$

beaker 1 (containing freezing mixture) and other in beaker 3 (containing hot water). You will observe that in beaker 1, the intensity of colour decreases whereas in beaker 3, intensity of colour increases.

$$\underset{\text{Red brown}}{2NO_2\,(g)} \rightleftharpoons \underset{\text{Colourless}}{N_2O_4\,(g)},\ \Delta_r H = -57.2 \text{ kJ mol}^{-1}$$

This is very easy to understand. At low temperature N_2O_4 is favoured (intensity of colour decreases) and at higher temperature, NO_2 is favoured (intensity of colour increases).

Effect of temperature can also be demonstrated by the following endothermic reaction :

$$\underset{\text{Pink}}{[Co(H_2O)_6]^{2+}\,(aq)} + 4Cl^-\,(aq) \rightleftharpoons \underset{\text{Blue}}{CoCl_4^{2-}\,(aq)} + 6H_2O$$

$$\Delta_r H = +\text{ve}$$

At room temperature, the equilibrium mixture is blue due to the presence of $CoCl_4^{2-}$. When cooled in a freezing mixture, the colour of the mixture changes to pink due to $[Co(H_2O)_6]^{2+}$.

The effect of temperature may be summed up as follows :

Increase in temperature —(Shifts the equilibrium in the direction of)→ **Endothermic reaction**

Decrease in temperature —(Shifts the equilibrium in the direction of)→ **Exothermic reaction**

3. Effect of Change of Pressure

The change of pressure has also an important effect on equilibrium of reactions which involve gaseous substances and there is change in total number of moles of gases in reactants and products. According to Le-Chatelier's principle, *increase of pressure on a system at equilibrium will shift the equilibrium in the direction in which pressure is reduced*. Now, as the pressure of the gaseous system is increased the volume occupied by the system decreases so that total number of moles per unit volume increases. To undo this stress, the reaction which produces small number of moles of gaseous substances will be favoured so that the increased pressure is reduced. This can be explained with the help of the following reaction :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

On increasing pressure, the volume occupied by the system will decrease. As a result, there will be a large number of moles of gaseous substance per unit volume. The effect of increased pressure can be undone if the equilibrium shifts in the direction which produces lesser number of gaseous moles. Since number of moles of the products (two) are less than those of the reactants (four), the equilibrium will shift in the direction of forward reaction in the above case. Therefore, more ammonia is formed.

If the products involve more number of gaseous moles than the reactants, as in the reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

the increase in pressure will favour the backward reaction.

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If there is no change in the number of moles of gaseous reactants and products, the pressure will have no effect on the equilibrium.

For example, in the following reactions, pressure does not alter the equilibrium :

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

It may be noted that in applying Le-Chatelier's principle to a heterogeneous equilibrium, the effect of pressure changes on solids and liquids can be ignored because the volume (and concentration) of a solution or liquid is nearly independent of pressure.

For example, in the reaction,

$$C(s) + CO_2(g) \rightleftharpoons 2\,CO_2(g)$$

When the pressure is increased, the reaction goes in the backward direction because number of moles of gas are less in the reactants side.

Effect of Pressure: An Illustrative Experiment

Let us consider the following exothermic reaction:

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

In this reaction, four mol of reactant gases ($CO + 3H_2$) become 2 mol of product gases ($CH_4 + H_2O$). Suppose the equilibrium mixture is kept in a cylinder fitted with a piston. Suppose at constant temperature it is compressed to one half of its original volume. Then total pressure will become double (according to pV = constant). Therefore, the partial pressure or concentrations of reactants and products have changed and the reaction mixture is no longer at equilibrium. According to Le-Chatelier's principle, since the pressure has doubled, the equilibrium will shift in forward direction in which number of moles of the gas or pressure decreases (pressure is proportional to the moles of the gas). This has been shown in Fig. 16.

This can also be understood by using reaction quotient, Q_c. Let the molar concentrations of different species at equilibrium be [CO], [H_2], [CH_4] and [H_2O]. When the volume of the reaction mixture is halved, the partial pressure and the concentration are doubled. We can obtain the reaction quotient by replacing each equilibrium concentration by double its value as :

$$Q_c = \frac{(2[CH_4])(2[H_2O])}{(2[CO])(2[H_2])^3}$$

$$= \frac{4}{16}\frac{[CH_4][H_2O]}{[CO][H_2]^3} = \frac{K_c}{4}$$

or $Q_c < K_c$

Since Q_c is less than K_c, the reaction proceeds in the forward direction.

The effect of pressure may be summed up as follows :

Increase in pressure —(Shifts the equilibrium in the direction of)→ **Lesser number of gaseous moles**

Decrease in pressure —(Shifts the equilibrium in the direction of)→ **Larger number of gaseous moles**

4. Effect of Volume Change

We know that increase in pressure means decrease in volume, so the effect of change of volume will be exactly reverse to that of pressure. Thus, decreasing the volume of a mixture of gases at equilibrium shifts the equilibrium in the direction of lesser number of gaseous molecules while increasing the volume shifts the equilibrium in the direction of large number of gaseous molecules.

5. Effect of Catalyst

Catalyst has no effect on equilibrium. This is because, catalyst favours the rate of forward and backward reactions equally. It simply helps to achieve the equilibrium quickly. It may also be noted that a catalyst has no effect on the equilibrium composition of a reaction mixture. Consider, for example, the reaction of SO_2 to SO_3. It is industrially very important in the manufacture of H_2SO_4 by **Contact process.**

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\quad K_c = 1.7 \times 10^{26}$

According to the value of K_c, reaction should go to completion. But oxidation of SO_2 to SO_3 is a slow process and it does not give a significant amount of SO_3 even after keeping the reactants in contact for a

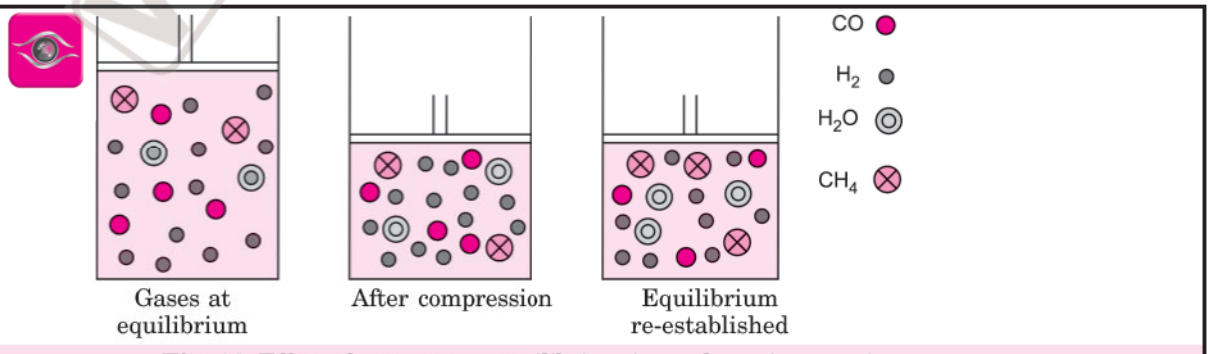

Fig. 16. Effect of pressure on equilibrium in methanation reaction.

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long time. However, in the presence of platinum or of vanadium pentoxide (V_2O_5) as catalyst, the rate of reaction becomes quite appreciable. It may be noted that if a reaction has an exceedingly small value of equilibrium constant, a catalyst would be of little help.

Catalyst does not shift the equilibrium in any direction

6. Effect of addition of inert gas

The addition of an inert gas (like helium, neon, etc.) has the following effects on the equilibrium depending upon the conditions :

***(i)* Addition of an inert gas at constant volume.** When an inert gas is added to the equilibrium system at constant volume, then the total pressure will increase. But the concentrations of the reactants and products (ratio of their moles to the volume of the container) will not change. Hence, under these conditions, *there will be no effect on the equilibrium.*

***(ii)* Addition of an inert gas at constant pressure.** When an inert gas is added to the equilibrium system at constant pressure, then the volume will increase. As a result, the number of moles per unit volume of various reactants and products will decrease. Hence, *the equilibrium will shift in a direction in which there is increase in number of moles of gases.* For example, for an equilibrium,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

the addition of an inert gas at constant pressure will shift the equilibrium to the backward direction. On the other hand, for the equilibrium,

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

the addition of an inert gas at constant pressure will shift the equilibrium to the forward direction.

However, addition of an inert gas at constant pressure for the equilibrium reaction :

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

will have no effect because the number of moles of reactants and products are same.

APPLICATIONS OF LE-CHATELIER'S PRINCIPLE OF PHYSICAL EQUILIBRIA

Le-Chatelier's principle is applicable not only to chemical equilibria but also to physical equilibria in a similar way. Let us discuss physical equilibria,

***(a)* Dissolution of ammonium chloride in water.** Ammonium chloride dissolves in water with the absorption of heat.

$$NH_4Cl(s) + H_2O \rightleftharpoons NH_4^+(aq) + Cl^-(aq); \quad \Delta H = +ve$$

If the temperature of a saturated solution of ammonium chloride is increased, then the equilibrium shifts in the direction to counteract the effect of increased temperature. According to Le-Chatelier's principle, the solubility of ammonium chloride will increase with rise in temperature. Thus, it may be concluded that **the solubility of all substances which dissolve with absorption of heat will increase with rise in temperature.**

***(b)* Dissolution of sodium hydroxide in water.** Sodium hydroxide dissolves in water with the evolution of heat. Therefore, the solubility of sodium hydroxide will decrease with rise in temperature.

$$NaOH(s) + H_2O \rightleftharpoons Na^+(aq) + OH^-(aq); \quad \Delta H = -ve$$

Thus, **the solubility of substances which dissolve with evolution of heat will decrease with rise in temperature.**

***(c)* Solubility of gas in liquid.** Suppose there is an equilibrium between the gas and its solution in a cylinder. Now, when the pressure is increased by compressing the system with the help of a piston, the volume of the system decreases. Consequently, the system proceeds in a direction in which the pressure of the gas decreases and therefore, some of the gas dissolves in solution. Thus, increase of pressure increases the solubility of a gas in liquids while decrease in pressure reduces the solubility. For example, during the preparation of carbonated drinks such as Campa Cola or Beer, a large amount of CO_2 is dissolved in the solution under high pressure. On the other hand, when the bottle of Campa Cola or beer is opened, the pressure is decreased and the dissolved carbon dioxide escapes out.

Le-Chatelier's principle is quite useful to find out the favourable conditions of concentration, temperature and pressure for some reversible reactions of industrial importance.

SOLVED EXAMPLES

Example 36.

Consider the reaction :

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 189.4\ kJ.$$

Indicate the direction in which the equilibrium will shift when

(i) temperature is increased

(ii) volume is increased

(iii) a catalyst is added

(iv) pressure is decreased

(v) concentration of SO_2 is increased

(vi) helium gas is added at constant volume so that the total pressure is increased

(vii) helium gas is added at constant pressure.

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Solution: *(i) Temperature is increased.* The equilibrium will shift to the backward direction as the increase in temperature will be compensated by absorbing heat.

(ii) Volume is increased. The equilibrium will shift to the left. On increasing volume of the container, it results in more space between the molecules. This stress will be relieved by the formation of more molecules (for every 2 molecules of SO_3, three molecules *i.e.,* two of SO_2 and one of O_2 are produced).

(iii) A catalyst is added. The equilibrium will not shift in any direction because both the forward and backward rates are increased to the same extent.

(iv) Pressure is decreased. The equilibrium will shift to the left to produce more number of moles.

(v) Concentration of SO_2 is increased. The equilibrium will shift to the right so that additional SO_2 is used up to form SO_3

(vi) Helium gas is added at constant volume so that the total pressure is increased. The volume of the container and the concentration of the reacting molecules are constant. The addition of inert gas will cause the increase in the total pressure of the system. Therefore, there will be no effect on the equilibrium.

(vii) Helium gas is added at constant pressure. When helium gas is added to the system at constant pressure, it will result in increase in volume. As a result, the number of molecules per unit volume will decrease. This stress is relieved by the formation of more molecules and the equilibrium will shift to the left (three molecules are produced for every two molecules of SO_3 decomposed).

❑ Example 37.

Hydrogen gas is obtained from natural gas by partial oxidation with steam as per following exothermic reaction

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

(a) Write an expression for K_p for the reaction.

(b) How will the value of K_p and composition of equilibrium mixture be affected by

(i) increasing the pressure

(ii) increasing the tempertaure

(iii) using a catalyst. **N.C.E.R.T.**

Solution:

(a) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

$$K_p = \frac{(p_{CO}) \times (p_{H_2})^3}{(p_{CH_4}) \times p_{H_2O}}$$

(b) (i) According to Le-Chatelier's principle, with increass in pressure equilibrium will shift to the left to produce less number of moles.

(ii) Since the reaction is exothermic, with increases in temperature equilibrium will shift to the backward direction (endothermic reaction)

(c) Equilibrium will not be disturbed by using a catalyst. However, equilibrium will be attained quickly.

Practice Problems

43. In the manufacture of ammonia as

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g);\ \Delta H = -93.8\ kJ$$

Work out the conditions for maximum yield of ammonia (Apply Le-Chatelier's principle).

44. For the reaction

$$2NO(g) \rightleftharpoons N_2(g) + O_2(g);\ \Delta H = -ve$$

$K = 2.5 \times 10^{20}$ at 298 K. What will happen to concentration of N_2 if

(i) concentration of NO is increased

(ii) temperature is decreased to 273 K

(iii) pressure is reduced ?

45. At 473 K, equilibrium constant, K_c for the decomposition of PCl_5 is 8.3×10^{-3}. If the decomposition is predicted as :

$$PCl_5(s) \rightleftharpoons PCl_3(g) + Cl_2(g);\quad \Delta_r H^{\ominus} = 124.0\ kJ\ mol^{-1}$$

(a) Write an expression for K_c for the reaction.

(b) What is the value of K_c for the reverse reactions oat the same temeprature ?

(c) What would be the effect on K_c if

(i) more PCl_5 is added

(ii) the pressure is inceased

(iii) the temperature is increased

46. In which of the following reactions, increase in temperature as well as decrease in pressure shift the equilibrium towards the forward direction :

(i) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $\Delta H = +ve$

(ii) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = +ve$

(iii) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -ve$

(iv) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +ve$

47. Consider the following equilibrium reaction :

$$[CoCl_4]^{2-} + 6H_2O \rightleftharpoons [Co(H_2O)_6]^{2+} + 4Cl^-$$

Blue Pink

The colour of the solution is blue. What will be the colour change when water is added to the system at equilibrium ?

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48. Using Le-Chatelier's principle, predict which conditions of temperature and pressure would give high yield of products in the following reactions :

(*i*) $CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $\Delta H = +41$ kJ

(*ii*) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -198$ kJ

(*iii*) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = 175$ kJ

49. In reaction :

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH$; $\Delta_r H^{\ominus} = -92.0$ kJ mol^{-1}

Concentration of hydrogen, carbon monoxide and methanol become constant at equilibrium. What will happen if

(*i*) Volume of reaction vessel in which reactants and products are contained is suddenly reduced to half

(*ii*) the partial pressure of hydrogen is suddenly doubled

(*iii*) An inert gas is added to the system ?

N.C.E.R.T.

50. Which of the following reactions will get affected by increase of pressure ? Also predict whether the change will cause the reaction to go into the right or left direction ?

(*i*) $C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$

(*ii*) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

(*iii*) $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$

(*iv*) $CH_4(g) + 2S_2(g) \rightleftharpoons CS_2(g) + 2H_2S(g)$

Answers to Practice Problems

43. (*i*) increase in concentration of N_2 and H_2
(*ii*) increase in pressure
(*iii*) decrease in temperature
(*iv*) addition of catalyst

44. (*i*) increases (*ii*) increases (*iii*) no change

45. (*a*) $K_c = \dfrac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(s)]}$

(*b*) $\dfrac{1}{8.3\times10^{-3}} = 1.20 \times 10^2$

46. (*i*) and (*iv*)

47. Blue solution becomes pink.

49. $\dfrac{[CH_3OH]}{[CO][H_2]^2}$ and $K_p = \dfrac{p_{CH_3OH}}{p_{CO} \times p_{H_2}^{\ 2}}$

(*i*) When volume of the vessel is reduced to half, the concentration of the species becomes double.

$$Q_c = \frac{2[CH_3OH]}{2[CO](2[H_2])^2} = \frac{1}{4}K_c$$

As $Q < K_c$, equilibrium will shift in the forward direction producing more of CH_3OH.

(*ii*) When pH_2 is made double, then

$$Q_p = \frac{pCH_3OH}{p_{CO} \times (2p_{H_2})^2} = \frac{1}{4}K_p$$

As $Q_c < K_p$ equilibrium will shift in the foward direction.

(*iii*) As volume remains constant, molar concentration will not change. Hence, no effect on equilibrium state.

50. (*i*) right (*ii*) left (*iii*) left (*iv*) no effect.

add on Conceptual Questions 1

Q. 1. What happens to rate of forward and rate of backward reaction when the equilibrium is attained ?

Ans. The rate of forward reaction becomes equal to rate of backward reaction at equilibrium.

Q. 2. What happens to an equilibrium in a reversible reaction if a catalyst is added to it ?

Ans. When catalyst is added, the state of equilibrium is not disturbed but equilibrium is attained quickly. This is because the catalyst increases the rate of forward and backward reaction to the same extent.

Q. 3. The equilibrium constant for the reaction :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

is K. What will be the equilibrium constant for the reaction involving decomposition of one mole of ammonia ?

Ans. The decomposition of ammonia may be expressed as:

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

Equilibrium constant will be = $\dfrac{1}{\sqrt{K}}$.

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CONCEPTUAL QA

Q. 4. A system is in equilibrium as :

$$SO_2Cl_2 + \text{Heat} \rightleftharpoons SO_2 + Cl_2$$

Why does the temperature of the system increase when Cl_2 is added to the equilibrium mixture at constant volume ?

Ans. When Cl_2 is added to the equilibrium system, the reaction shifts to the left. This produces more heat and therefore, temperature is increased.

Q. 5. Why does solubility of CO_2 decrease with rise in temperature ?

Ans. $CO_2(g) + nH_2O \longrightarrow CO_2(aq)$

The process occurs with decrease in randomness. Since this reaction is feasible, it must be exothermic in the forward direction. Therefore, the increase of temperature pushes the reaction in the backward direction, thereby decreasing the solubility.

Q. 6. The equilibrium constants of a reaction at 27°C and 127°C are 1.6×10^{-3} and 7.6×10^{-2} respectively. Is the reaction exothermic or endothermic ?

Ans. As the equilibrium constant has increased with increase in temperature, the reaction is endothermic in the forward direction.

Q.7. The equilibrium constants for the reactions :

$$N_2 + O_2 \rightleftharpoons 2NO$$

$$2NO + O_2 \rightleftharpoons 2NO_2$$

are K_1 and K_2 respectively. What will be the equilibrium constant for the reactions :

(*i*) $N_2 + 2O_2 \rightleftharpoons 2NO_2$ **and**

(*ii*) $2NO_2 \rightleftharpoons N_2 + 2O_2$

Ans. For reaction (*i*) , $K = K_1 \times K_2$

For reaction (*ii*) , $K = 1/K_1 \times K_2$

Q. 8. What does the equilibrium constant K less than 1 indicate ?

Ans. This indicates that the reaction does not proceed much in the forward direction.

Q. 9. For an exothermic reaction, what happens to the equilibrium constant if temperature is raised?

Ans. For an exothermic reaction, K_b will increase with rise in temperature much more than K_f. As a result, $\frac{K_f}{K_b}$ will decrease.

Q.10. What is the name for a type of reaction that does not go all the way to completion but reaches an equilibrium ?

Ans. Reversible reaction.

Q.11. Write expressions for K_p and K_c for the decomposition reaction of calcium carbonate.

Ans. The reaction is :

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K_c = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$$

Taking active masses of solids to be unity

$$K_c = [CO_2(g)]$$

$$K_p = pCO_2$$

Q.12. The equilibrium constants for the three reactions :

$$A + 2B \rightleftharpoons C, \quad K = 10^{-12}$$

$$3B + 2C \rightarrow D, \quad K = 10^{4}$$

$$A + 3B \rightarrow E, \quad K = 10^{9}$$

In which case, the yield of products will be maximum ?

Ans. Higher value of K means that the reaction has proceeded to a large extent in the forward direction. Thus, the maximum yield will in the third case ($K = 10^9$) *i.e.,* of product E.

Q.13. Why does the dissociation of PCl_5 decrease in the presence of Cl_2 ?

Ans. PCl_5 dissociates as :

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

In the presence of Cl_2 (one of the products), the equilibrium will shift in the backward direction. Therefore, the dissociation of PCl_5 decreases.

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Q.14. The equilibrium constant for the reaction :

$$SO_3\,(g) \rightleftharpoons SO_2\,(g) + \frac{1}{2}\,O_2\,(g) \text{ is 0.18 at 900 K}$$

What will be the equilibrium constant for the reaction :

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons SO_3\,(g)$$

Ans. K for the required reaction will be

$$K = \frac{1}{(0.18)^2} = 30.86 \text{ mol L}^{-1}$$

Q.15. Will the yield of C or F increases with increase in temperature ?

$$A + 2B \longrightarrow C \qquad \Delta H = +\text{ve}$$
$$2D + E \longrightarrow F \qquad \Delta H = -\text{ve}$$

Ans. Yield of C will increase with increase in temperature because according to Chatelier principle, endothermic reaction is forward with increase in temperature.

Q.16. At 500 K, K_c for the reaction :

$$H_2\,(g) + D_2\,(g) \rightleftharpoons 2HD\,(g) \text{ is 3.6}$$

What is the value of K_c for

$$2HD\,(g) \rightleftharpoons H_2\,(g) + D_2\,(g)$$

Ans. K_c will be $\frac{1}{3.6} = 0.28$.

Q.17. At 450 K, $K_p = 2.0 \times 10^{10}$/bar for the given reaction at equilibrium :

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What is the K_c at this temperature ? ***N.C.E.R.T.***

Ans. $K_p = K_c\,(RT) \quad \text{or } K_c = \frac{K_p}{(RT)^{\Delta n_g}}$

$\Delta n_g = 2 - (2 + 1) = -1$, T = 450 K, R = 0.083 L bar K^{-1} mol^{-1}

$$\therefore \quad K_c = \frac{2.0\times10^{10}}{(0.083\times450)^{-1}} = 2.0 \times 10^{10} \times (0.083 \times 450)$$
$$= 7.47 \times 10^{11}\ M^{-1}$$

Q.18. Does the number of moles of reaction product increase, decrease or remain same when each of the following equilibrium is subjected to a decrease in pressure by increasing volume ?

(a) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(b) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

(c) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$ ***N.C.E.R.T.***

Ans. (a) increase (b) decrease (c) remain same.

Q.19. Which of the following reaction will get affected by increasing the pressure ? Also mention whether change will cause the reaction to go into forward or backward direction ?

(i) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

(ii) $CH_4(g) + 2S_2(g) \rightleftharpoons CS_2(g) + 2H_2S(g)$

(iii) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

(iv) $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

(v) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(vi) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ ***N.C.E.R.T.***

Ans. (i) backward direction (ii) no effect
(iii) backward direction (iv) forward direction
(v) backward direction. (vi) backward direction.

Q.20. At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as :

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)\ \Delta_r H^\circ = 124.0 \text{ kJ mol}^{-1}.$$

(a) Write an expression for K_c of the reaction

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(*b*) What is the value of K_c for reverse reaction at the same temperature ?

(*c*) What would be the effect on K_c if

(*i*) more PCl_5 is added

(*ii*) pressure is increased

(*iii*) temperature is increased ? ***N.C.E.R.T.***

Ans. (*a*) $K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]}$

(*b*) K_c (reverse) $= \dfrac{1}{8.3\times10^{-3}} = 120.48$

(*c*) (*i*) No effect because K_c is constant at a given temperature

(*ii*) No effect

(*iii*) increases. Since reaction is endothermic, on increasing temperature, k_f will increase so that $K_c = k_f / k_b$ will also increase.

Q.21. Predict which of the following reaction will have appreciable concentration of reactants and products :

(*a*) $Cl_2(g) \rightleftharpoons 2Cl(g)$ $K_c = 5 \times 10^{-39}$

(*b*) $Cl_2(g) + 2NO(g) \rightleftharpoons 2NOCl(g)$ $K_c = 3.7 \times 10^{8}$

(*c*) $Cl_2(g) + 2NO_2(g) \rightleftharpoons 2NO_2Cl(g)$ $K_c = 1.8$ ***N.C.E.R.T.***

Ans. (*a*) Reactants predominate (*b*) Products predominate (*c*) both reactants and products will be present in comparable amounts.

Q.22. The value of K_c for the reaction :

$3O_2(g) \rightleftharpoons 2O_3(g)$ is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2}, what is the concentration of O_3 ? ***N.C.E.R.T.***

Ans.
$$K_c = \frac{[O_3]^2}{[O_2]^3}$$

$$2.0 \times 10^{-50} = \frac{[O_3]^2}{(1.6\times10^{-2})^3}$$

or
$$[O_3]^2 = 2.0 \times 10^{-50} \times (1.6 \times 10^{-2})^3 = 8.192 \times 10^{-56}$$

$$[O_3] = 2.86 \times 10^{-28}\ M$$

Q.23. Explain why pure solids and liquids are ignored while writing the equilibrium constant expression. ***N.C.E.R.T.***

Ans. For the concentration of pure solid or pure liquid,

$$[\text{Solid}] \text{ or } [\text{Liquid}] = \frac{\text{No. of moles}}{\text{Volume in L}} = \frac{\text{Mass/ Molar mass}}{\text{Volume}}$$

$$= \frac{\text{Mass}}{\text{Volume}} \times \frac{1}{\text{Molar mass}} = \text{Density} \times \frac{1}{\text{Molar mass}}$$

Since density of pure solid or liquid is constant at constant temperature and molar mass is also constant therefore, their molar concentrations are constant and are included in the equilibrium constant.

Q.24. What will be the effect on equilibrium of the following reaction :

$2N_2O\ (g) + O_2\ (g) \rightleftharpoons 4NO\ (g)$; $\Delta H > 0$

(*i*) When volume of vessel increases

(*ii*) Temperature decreases?

Ans. (*i*) When volume of vessel increases, pressure will decrease. As the forward reaction is accompanied by increase in number of moles, the decrease in the pressure will favour forward reaction (according to Le-Chatelier principle).

(*ii*) As ΔH is + ve, the reaction is endothermic, decrease of temperature will favour the direction in which heat is released *i.e.*, backward reaction.

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Advanced Level PROBLEMS *Accelerate Your Potential (for JEE Advance)*

Problem 1. **An equilibrium mixture at 300 K contains N_2O_4 and NO_2 at 0.28 and 1.1 atm pressure respectively. If the volume of the container is doubled, calculate the new equilibrium pressure of two gases.**

Solution.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Pressure at equilibrium 0.28 1.1

$$K_p = \frac{p(NO_2)^2}{p(N_2O_4)} = \frac{(1.1)^2}{(0.28)} = 4.32 \text{ atm}$$

If volume of the container is doubled, the pressure will be reduced to half.

$$N_2O_4 \rightleftharpoons 2NO_2$$

New pressure $\left(\frac{0.28}{2} - p\right)$ $\left(\frac{1.1}{2} + 2p\right)$

$$K_p = \frac{\left(\frac{1.1}{2} + 2p\right)^2}{\left(\frac{0.28}{2} - p\right)} = 4.32$$

Solving $p = 0.045$

$\therefore$ $p(N_2O_4) = 0.14 - 0.045 = \mathbf{0.095 \text{ atm}}$

$p(NO_2) = 0.55 + 2(0.045) = \mathbf{0.64 \text{ atm}}$

Problem 2. **When 3.06 g of solid NH_4HS is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.**

(*i*) Calculate K_c and K_p for the reaction at 27°C.

(*ii*) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask ?

Solution. Moles of NH_4HS introduced into the flask

$$= \frac{3.06}{51} = \mathbf{0.06}$$

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

Initial conc. 0.06 0 0

Equi. conc. 0.06 $(1 - x)$ 0.06 x 0.06 x

Since x is 30% *i.e.*, = 0.3

At. equi. 0.06 $(1 - 0.3)$ 0.06 × 0.3 0.06 × 0.3

0.042 0.018 0.018

Vol. of flask = 2 L

$$[NH_3] = \frac{0.018}{2} = 0.009$$

$$[H_2S] = \frac{0.018}{2} = 0.009$$

$$K_c = [NH_3]\,[H_2S]$$

$$= 0.009 \times 0.009 = 8.1 \times 10^{-5}$$

$$K_p = K_c (RT)^{\Delta n_g}$$

$$\Delta n_g = 1 + 1 - 0 = 2$$

$$K_p = 8.1 \times 10^{-5} \times (0.082 \times 300)^2$$

$$= \mathbf{0.049.}$$

(*ii*) Addition of NH_4HS does not change the position of equilibrium because K_c does not depend upon the amount of $NH_4HS(s)$.

Problem 3. **At 817° C, K_p for the reaction between CO_2 (*g*) and excess hot graphite (*s*) is 10 atm.**

(*a*) What are the equilibrium concentrations of the gases at 817° C and a total pressure of 5 atm ?

(*b*) At what total pressure, the gas contains 5% CO_2 by volume ?

Solution.

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Initial moles 1 0

Moles at equi. $1 - \alpha$ 2α

(α is the degree of dissociation)

Total moles = $1 - \alpha + 2\alpha = 1 + \alpha$

Partial pressure of CO_2, $p(CO_2) = \left(\frac{1-\alpha}{1+\alpha}\right) \times 5$

Partial pressure of CO, $p(CO) = \left(\frac{2\alpha}{1+\alpha}\right) \times 5$

$$K_p = \frac{p(CO)^2}{p(CO_2)}$$

$$10 = \frac{\left(\frac{2\alpha}{1+\alpha} \times 5\right)^2}{\left(\frac{1-\alpha}{1+\alpha} \times 5\right)}$$

$$= \frac{20\alpha^2}{1-\alpha^2}$$

or $20\alpha^2 = 10 - 10\alpha^2$

$30\alpha^2 = 10$

$\therefore$ $\alpha = \sqrt{\frac{1}{3}} = 0.577$

(*a*) At equilibrium

$\therefore$ Moles of $CO_2 = 1 - \alpha = 1 - 0.577 = \mathbf{0.423}$

Moles of $CO = 2\alpha = 2 \times 0.577 = \mathbf{1.154}$

(*b*) % of CO_2 = 5% by volume

% of CO = 95% by volume

Then $p(CO_2) = \frac{5}{100} \times p = 0.05\,p$

$$p(CO) = \frac{95}{100} \times p = 0.95\,p$$

$$K_p = \frac{(0.95\,p)^2}{(0.05\,p)} = 18.05\,p$$

or $10 = 18.05\,p$

$\therefore$ $p = \frac{10}{18.05} = \mathbf{0.554 \text{ atm.}}$

Problem 4. **Ammonium carbamate (NH_2COONH_4) decomposes as :**

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

In a closed vessel containing ammonium carbamate in equilibrium, ammonia is added such that partial pressure of NH_3 becomes equal to original total pressure. Calculate the ratio of final total pressure to the original pressure.

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Solution. Suppose the total pressure of the mixture initally is p. This is due to the partial pressure of NH_3 and CO_2 which are present in the ratio of 2:1.

$$p(NH_3) = \frac{2}{3}p \text{ and } p(CO_2) = \frac{1}{3}p$$

$$\therefore\ K_p = p(NH_3)^2 \times p(CO_2) = \left(\frac{2}{3}p\right)^2 \times \left(\frac{1}{3}p\right) = \frac{4}{27}p^3$$

After adding NH_3, $p(NH_3) = p$ (given)

$$\therefore\quad p^2 \times p(CO_2) = K_p = \frac{4}{27}p^3$$

$$\therefore\quad p(CO_2) = \frac{4}{27}p$$

$$\text{Final total pressure} = p(NH_3) + p(CO_2) = p + \frac{4}{27}p = \frac{31}{27}p$$

$\therefore$ Ratio of final total pressure to the original pressure **= 31:27**

Problem 5. A mixture of SO_2, O_2 and SO_3 gases are maintained in a 10L flask at a temperature at which $K_c = 100$ for the reaction,

$$SO_2 + O_2 \rightleftharpoons SO_3$$

(*i*) If the moles of SO_2 and SO_3 are equal in the flask, how much O_2 is present at equilibrium?

(*ii*) If the number of moles of SO_3 in the flask is twice the number of moles of SO_2, how much O_2 is present at equilbrium?

Solution. $2SO_2 + O_2 \rightleftharpoons 2SO_3$

$$K_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

(*i*) Let $[SO_2] = [SO_3] = x$

$$K_C = \frac{(x)^2}{(x)^2[O_2]} = 100$$

$$\therefore\quad [O_2] = \frac{1}{100} \text{ mol L}^{-1}$$

$$\text{Now}\quad [O_2] = \frac{\text{Moles of } O_2}{10} = \frac{1}{100} \text{ (volume = 10L)}$$

$$\therefore \text{ Moles of } O_2 = \frac{10}{100} = 0.1 \text{ mol}$$

(*ii*) Let moles of $SO_2 = y$, then moles of $SO_3 = 2y$

$$[SO_2] = \frac{y}{10},\ [SO_3] = \frac{2y}{10},\ [O_2] = ?$$

$$K_C = \frac{\left(\frac{2y}{10}\right)^2}{\left(\frac{y}{10}\right)^2[O_2]} = 100$$

$$\frac{4}{[O_2]} = 100 \text{ or } [O_2] = \frac{4}{100} = 0.04 \text{ mol L}^{-1}$$

$$\text{Now } [O_2] = \frac{\text{Moles of } O_2}{10} = 0.04$$

$\therefore$ Moles of $O_2 = 0.04 \times 10 = 0.4$ mol

Problem 6. The equilbrium constant of the reaction: $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ at 373K is 50. If a 1L flask containing 1 mol of A_2 is connected to a 2L flask containing 2 mol of B_2, how many moles of AB will be formed at 373K?

Solution. If x is the moles of A_2 converted to AB at equilibrium and the total volume is 1 + 2 = 3L

	A_2	+ B_2	$\rightleftharpoons$	2AB
Initial conc.	1	2		0
Moles at equ.	(1–x)	(2–x)		2x

$$[A_2] = \frac{1-x}{3},\ [B_2] = \frac{2-x}{3},\ [AB] = \frac{2x}{3}$$

$$K_c = \frac{[AB]^2}{[A_2][B_2]} = \frac{\left(\frac{2x}{3}\right)^2}{\left(\frac{1-x}{3}\right)\left(\frac{2-x}{3}\right)} = 50$$

$$\frac{4x^2}{(1-x)(2-x)} = 50$$

Solving for x, we get $x = 0.955$,

Moles of AB formed = $2 \times 0.955 = 1.91$ mol

Problem 7. At 800K, K_p for the reaction: $N_2O_4 \rightleftharpoons 2NO_2$ is 700 mm. Calculate the percentage dissociation of N_2O_4 at equilibrium pressure of 175 mm. At what pressure, the dissociation will be 50%?

Solution. Suppose initially N_2O_4 taken = 1 mol and its degree of dissociation is α.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial conc.	1		0
At equ.	1–α		2α

Total moles = $1-\alpha + 2\alpha = 1 + \alpha$

If p is the total pressure at equilibrium,

$$p(N_2O_4) = \frac{1-\alpha}{1+\alpha}.p$$

$$p(NO_2) = \frac{2\alpha}{1+\alpha}.p$$

$$K_p = \frac{p(NO_2)^2}{p(N_2O_4)} = \frac{\left(\frac{2\alpha}{1+\alpha}p\right)^2}{\left(\frac{1-\alpha}{1+\alpha}p\right)}$$

$$\text{or} = \frac{4\alpha^2}{(1+\alpha)(1-\alpha)}p = \frac{4\alpha^2}{1-\alpha^2}p$$

Putting, $K_p = 700$mm and equilibrium pressure, $p = 175$mm, we get

$$\frac{4\alpha^2}{1-\alpha^2} \times 175 = 700$$

$$\text{or}\quad \frac{4\alpha^2}{1-\alpha^2} = 4 \quad \text{or} \quad \frac{\alpha^2}{1-\alpha^2} = 1$$

$$\text{or}\quad \alpha^2 = 1-\alpha^2 \text{ or } 2\alpha^2 = 1$$

$$\text{or}\quad \alpha^2 = 0.5$$

$$\therefore\quad \alpha = 0.707$$

$$\text{or}\quad \alpha = \mathbf{70.7\%}$$

Now, for dissociation to be 50%, $\alpha = 0.50$, $K_p = 700$mm

Let p' be the equilibrium pressure

$$\frac{4\times(0.5)^2}{1-(0.5)^2}p' = 700$$

$$\frac{4\times(0.25)}{1-(0.25)}p' = 700$$

$$1.33p' = 700$$

$$\text{or}\quad p' = 700 \times 1.33 = \mathbf{526.3\ mm}$$

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PART B : IONIC EQUILIBRIUM IN SOLUTIONS

IONIC EQUILIBRIUM

Chemical reactions in solutions play very important role in chemistry. For example, sodium chloride does not conduct electricity in the solid state. However, when it is dissolved in water, it becomes good conductor of electricity. Michael Faraday classified the substances into two types : *electrolytes* and *non-electrolytes.*

The substances which conduct electricity in their molten states or in the form of their aqueous solutions are called electrolytes. For example, *acids, bases* and *salts* are electrolytes. On the other hand, ***the substances which do not conduct electricity in the molten states or in the form of their aqueous solutions are called*** **non-electrolytes.** The substances like sugar, urea, glycerine, etc. are non-electrolytes.

When an electrolyte is dissolved in water, it splits up into ions. For example, sodium chloride in the solid state exists as a collection of positively charged sodium ions (cations) and negatively charged chloride ions (anions). These are held together by strong electrostatic forces of attraction in the solid state. Due to these strong attractive forces, the ions do not move freely and therefore, do not conduct electricity in the solid state. When such a compound is dissolved in water, a high dielectric constant of water cuts down the forces of attraction between the ions. As a result, the ions get separated and dissolve in water. There is an another concept of ionisation. We know that water is a polar molecule. As oxygen is more electronegative than hydrogen, the oxygen atom acquires some partial negative charge and hydrogen atoms get positive charge. When an electrolyte (say NaCl) is dissolved in water, the polar water molecules arrange themselves around the ions. Around the positively charged Na^+ ions, the water molecules arrange themselves with their negative poles facing the ions while around the negatively charged Cl^- ions, they arrange themselves with their positive poles facing the ions. This is shown in Fig. 17. Due to the forces of attraction between the ions and the water molecules, the electrostatic forces which bind the ions into a definite arrangement are weakened. Therefore, the ions are set free from the crystals and are dragged into the solution. The resulting ions in solution remain surrounded by water molecules and are said to be **hydrated.** This hydration of ions with water molecules stabilizes them.

The forces of attraction between oppositely charged ions are inversely proportional to the dielectric constant of the medium. ***The greater the dielectric constant, the greater is the dissolving power of the solvent.*** The dielectric constant of water is 80 and therefore, these forces are reduced by a factor of about 80 in aqueous solution and ions become free to move.

It is found that sodium chloride is almost completely ionised. However, all the substances do not ionize to the same extent. The degree of ionization depends upon the polarity and the strength of the bond and the extent of solvation of the ions formed. Depending upon the extent of ionisation; the electrolytes are divided into two classes : *strong electrolytes* and *weak electrolytes.*

(i) **Strong electrolytes.** *The substances which ionise almost completely into ions in aqueous solution* are called **strong electrolytes.** For example, HCl, H_2SO_4, HNO_3, NaOH, KOH, NaCl, KNO_3, etc. are strong electrolytes.

It may be noted that the equation for the ionisation reactions of strong electrolytes are written with only *single headed arrow directed to the right.* For example,

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$
$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$

(ii) **Weak electrolytes.** *The substances which ionise to a small extent in aqueous solution are* called **weak electrolytes.** For example, CH_3COOH, NH_4OH, $(NH_4)_2CO_3$, HCN, etc. are weak electrolytes.

In such cases, the molecules are in equilibrium with their ions. The ionisation of such electrolytes is written with double headed arrows. For example,

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The strong electrolytes are almost completely

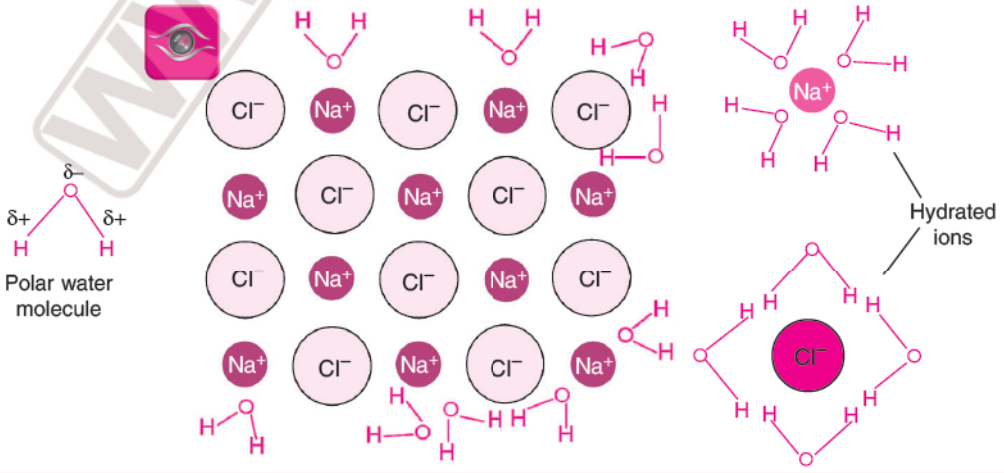

Fig. 17 Process of dissolution of sodium chloride in water.

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ionised. The unionised molecules are present to such a small extent that it is not of any significance to study the ionisation constant of strong electrolytes. However, the weak electrolytes are only partially ionised and a dynamic equilibrium is established after some time between the ions and the unionised molecules. This is called ***ionic equilibrium.*** Thus, the ***ionic equilibrium*** is the

equilibrium which is established between the unionised molecules and the ions in solution of weak electrolytes.

KEY NOTE

Difference between dissociation and ionisation

- **Dissociation** refers to the process of separation of ions already present in the solid state of solute when dissolved in water or a solvent. For example, dissociation of sodium chloride in water.
- **Ionisation** refers to the process in which a neutral molecule which does not contain ions splits into charged ions when dissolved in water or a solvent. For example, ionisation of a neutral molecule such as HCl in water.

➢ **However, the two terms are commonly used without any difference.**

ACID-BASE CONCEPTS

Long before the development of modern chemistry, attempts have been made to explain acids and bases. The earlier definitions were based mainly on the observable properties such as taste, their effect on other substances, etc.

According to earlier views, **acids** *were substances that tasted sour, changed the colour of litmus paper from blue to red, soluble in water and react with certain metals to give hydrogen gas,* etc. **Bases** *were substances that tasted bitter, have soapy feel, change the colour of litmus paper from red to blue and neutralize acids.*

In 1884, Ar Svante Arrhenius, a Swedish chemist, proposed a new theory of acids and bases known as *Arrhenius concept of acids and bases.* Now, there are three main concepts regarding acids and bases. These are :

1. Arrhenius Concept of Acids and Bases

According to **Arrhenius concept** (1887)

an acid is a substance which dissociates in aqueous solution to give hydrogen ions, $H^+(aq)$ **and** ***base is a substance which dissociates in aqueous solution to give hydroxyl ions, $OH^-(aq)$.***

Thus, according to Arrhenius, the acidic properties of a substance in aqueous solution are due to the presence of hydrogen ions H^+ (aq) and the basic properties of a substance in aqueous solution are due to the presence of hydroxyl ions, OH^- (aq). Thus, the ionisation of an acid, HX in water can be represented by the following equations :

$$HX(aq) \longrightarrow H^+(aq) + X^-(aq)$$

or $$HX(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + X^-(aq)$$

Similarly, the ionization of a base, MOH may be written as :

$$MOH(aq) \longrightarrow M^+(aq) + OH^-(aq)$$

For example, substances such as HCl, HNO_3, CH_3COOH, HCN, etc. are acids.

$$HCl \xrightarrow{\text{Water}} H^+(aq) + Cl^-(aq)$$

$$HNO_3 \xrightarrow{\text{Water}} H^+(aq) + NO_3^-(aq)$$

$$CH_3COOH \underset{}{\overset{\text{Water}}{\rightleftharpoons}} CH_3COO^-(aq) + H^+(aq)$$

On the other hand, the substances such as NaOH, KOH, NH_4OH, $Ca(OH)_2$, etc., are bases.

$$NaOH(aq) \xrightarrow{\text{Water}} Na^+(aq) + OH^-(aq)$$

$$NH_4OH \underset{}{\overset{\text{Water}}{\rightleftharpoons}} NH_4^+ + OH^-$$

$$Ca(OH)_2 \underset{}{\overset{\text{Water}}{\rightleftharpoons}} Ca^{2+}(aq) + 2OH^-(aq)$$

Thus, according to Arrhenius concept,

acids give H^+ ions in water while, bases give OH^- ions in water

The strength of an acid or a base depends upon its capacity of ionisation to H^+ or OH^- ion respectively. Acids such as HCl, HNO_3, H_2SO_4, etc. which are almost completely ionised in aqueous solution are called **strong acids** while acids such as CH_3COOH, HCN, etc. which are weakly ionised in aqueous solution are called **weak acids.**

Similarly, bases such as NaOH, KOH, etc. which are almost completely ionised in aqueous solution are called **strong bases** while bases such as NH_4OH, $Ca(OH)_2$, etc. which are only slightly ionised in aqueous solution are called **weak bases.**

Hydronium ion and Hydroxyl ions

Hydrogen ion, H^+ or proton has very small size (about 10^{-15} m radius) and intense electric field. Therefore, it readily binds to a water molecule at one of the two available lone pairs to form hydronium ion, H_3O^+. For example, when hydrogen chloride, HCl dissolves in water, it releases a hydrogen ion to a neighbouring water molecule as :

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

This species has been detected in many compounds such as H_3O^+, Cl^-, in the solid state. In aqueous solution, the hydronium ion is itself strongly hydrated in solution to give species like $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$. However, we shall use the simple formula H_3O^+ or H^+.

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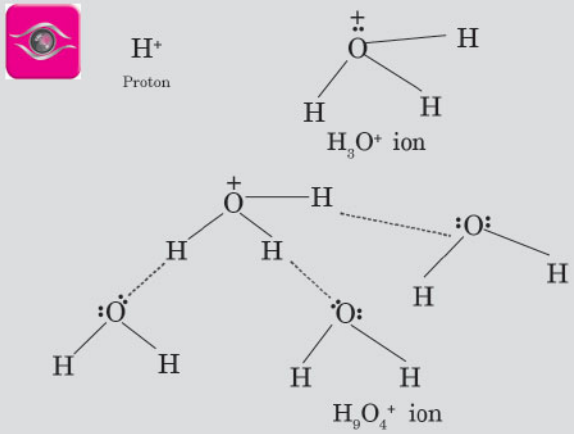


Similarly, the hydroxyl ion is hydrated to give species like $H_3O_2^-$, $H_5O_3^-$ and $H_7O_4^-$, etc.

2. Bronsted-Lowry Concept

The Arrhenius concept of acids and bases was extended further by Johannes Bronsted and Thomas M. Lowry (1923).

According to **Bronsted-Lowry concept,**

an acid is a substance which can donate proton (H^+) while a base is a substance which can accept a proton (H^+).

In other words, according to Bronsted-Lowry concept, **acid is a proton donor and base is a proton acceptor.** For example, in the following reaction, HCl loses a proton and is an acid whereas NH_3 accepts a proton and is a base.

$$HCl\,(aq) + NH_3\,(aq) \rightleftharpoons NH_4^+\,(aq) + Cl^-\,(aq)$$

The main advantage of this concept is that it is not restricted to neutral molecules. Rather, acids and bases can be either neutral molecules or ions. Some other examples of acids and bases are :

$$\underset{\text{acid}}{HCl(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

$$\underset{\text{acid}}{NH_4^+(aq)} + \underset{\text{base}}{H_2O\,(l)} \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{CO_3^{2-}(aq)} \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

$$\underset{\text{acid}}{NH_4^+(aq)} + \underset{\text{base}}{CH_3COO^-(aq)} \rightleftharpoons CH_3COOH(aq) + NH_3(aq)$$

The acid-base reactions are regarded as **proton transfer reactions.** There are certain substances such as H_2O, HCO_3^-, HSO_4^-, etc. which are capable of donating as well as accepting the proton. These substances are called **amphoteric substances.** For example, water behaves as an acid as well as base as illustrated below :

As a base :

$$\underset{\text{acid}}{HCl(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

As an acid :

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{NH_3(aq)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Similarly, bicarbonate ion (HCO_3^-) behaves as an acid and a base as :

$$\underset{\text{acid}}{HCO_3^-(aq)} + \underset{\text{base}}{NH_3(aq)} \rightleftharpoons NH_4^+(aq) + CO_3^{2-}(aq)$$

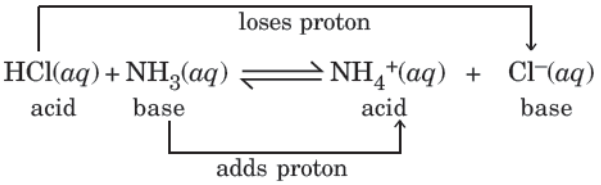
$$\underset{\text{acid}}{HCl(aq)} + \underset{\text{base}}{HCO_3^-(aq)} \rightleftharpoons H_2CO_3(aq) + Cl^-(aq)$$

NOTE

It may be noted that all **Arrhenius acids are also Bronsted acids but Arrhenius bases are not Bronsted bases.** According to Arrhenius concept, an acid is a substance which can give H^+ ions. According to Bronsted theory, an acid is a substance which can donate a proton. Hence, *all Arrhenius acids are also Bronsted acids.* However, there is a difference in the definition of base. According to the Arrhenius concept, a base is a substance which can donate OH^- ions and therefore, a base must be a source of OH^- ions in aqueous medium. But Bronsted theory requires a base to be a proton acceptor. Hence, **Arrhenius base may not be Bronsted base.** For example, NaOH is a base according to Arrhenius theory because it gives OH^- ions in aqueous solution but NaOH does not accept a proton as such. Thus, it may not be classified as a base according to Bronsted theory.

Conjugate Acid-Base Pairs

Consider a reaction of an acid and a base :



It is clear that HCl donates a proton (*acts as an acid*) and forms Cl^- ion which has a tendency to accept a proton (can act as a base). Similarly, NH_3 accepts a proton and acts as a base but it forms NH_4^+ ion which has a tendency to behave as an acid. In other words, an acid donates a proton and becomes a base and a base accepts a proton and becomes an acid.

The base formed from an acid is referred to as the **conjugate base of the acid.** Similarly, the acid formed from a base is called the **conjugate acid of the base.** Thus, in the above example, *Cl^- is the conjugate base of acid HCl and NH_4^+ is the conjugate acid of the base NH_3.*

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The pairs of acids and bases which are formed from each other by the gain or loss of a proton *are called* **conjugate acid-base pairs.**

Thus, Cl^-, HCl; NH_4^+ and NH_3 are conjugate acid-base pairs.

acid = conjugate base + H^+
base + H^+ = conjugate acid

Thus, *each conjugate acid has one extra proton and each conjugate base has one proton less.*

In general, each acid-base reaction involves two pairs of conjugate acids and bases. These are labelled as 1 and 2. Some examples are :

$Acid_1$		$Base_2$		$Acid_2$		$Base_1$
HNO_3	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NO_3^-
H_2SO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HSO_4^-
HCN	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CN^-
CH_3COOH	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CH_3COO^-
H_2O	+	NH_3	$\rightleftharpoons$	NH_4^+	+	OH^-
H_2O	+	CO_3^{2-}	$\rightleftharpoons$	HCO_3^-	+	OH^-
HCl	+	HCO_3^-	$\rightleftharpoons$	H_2CO_3	+	Cl^-

Relative Strengths of Conjugate Acids and Bases

According to Bronsted-Lowry concept, *the strength of an acid depends upon its tendency to donate a proton and the strength of a base depends upon its tendency to accept a proton.* According to this, a strong acid means a good proton donor and a strong base means a good proton acceptor. For example, consider the dissociation of HCl in water,

$$\underset{\text{Strong acid}}{HCl(aq) + H_2O(l)} \rightleftharpoons \underset{\text{Weak base}}{H_3O^+(aq) + Cl^-(aq)}$$

HCl has a strong tendency to donate a proton, therefore, it is a strong acid. But Cl^- ion has very little tendency to accept a proton, therefore, Cl^- ion is a weak base. Thus, the equilibrium lies towards right hand side. Thus, **conjugate base of a strong acid is a weak base.** Consider the dissociation of acetic acid.

$$\underset{\text{Weak acid}}{CH_3COOH(aq) + H_2O(l)} \rightleftharpoons \underset{\text{Strong base}}{CH_3COO^-(aq)} + H_3O^+(aq)$$

Now, acetic acid is a weak acid and the equilibrium lies towards left. This also indicates that CH_3COO^- ion has greater tendency to accept the proton and therefore, is a strong base.

Similarly, the strong base has a weak conjugate acid and a weak base has a strong conjugate acid. For example,

$$\underset{\text{Strong base}}{CH_3COO^-(aq) + H_3O^+(aq)} \rightleftharpoons \underset{\text{Weak acid}}{CH_3COOH(aq) + H_2O(l)}$$

$$\underset{\text{Weak base}}{Cl^-(aq) + H_3O^+(aq)} \rightleftharpoons \underset{\text{Strong acid}}{HCl(aq) + H_2O(l)}$$

To sum up
Strong acid has weak conjugate base
Weak acid has strong conjugate base
Strong base has weak conjugate acid
Weak base has strong conjugate acid

Thus, strong acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3), sulphuric acid (H_2SO_4) etc will give conjugate bases like ClO^-_4, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, etc, which are much weaker bases than H_2O. On the other hand, weak acids such as nitrous acid (HNO_2), hydrofluoric acid (HF), acetic acid (CH_3COOH), etc, give strong conjugate bases NO_2^-, F^-, CH_3COO^-, etc. which have good tendency to accept proton.

Advantages of Bronsted-Lowry Concept over Arrhenius Concept

(*i*) Bronsted Lowry concept can explain the basic character of substances like Na_2CO_3, NH_3, etc. (which do not contain OH^- group and hence were not bases according to Arrhenius concept) on the basis that they accept protons.

(*ii*) Bronsted Lowry concept is not limited to molecules but also covers even the ionic species to act as acids or bases.

(*iii*) Bronsted Lowry concept can explain the acid-base reactions in the non-aqueous medium also.

Limitations of Bronsted-Lowry Concept

Though Bronsted-Lowry concept has wider applications than Arrhenius concept, yet it has some limitations also.

(*i*) It cannot explain the reactions between acidic oxides like CO_2, SO_2, SO_3, etc. and basic oxides like CaO, BaO, MgO, etc. which take place even in the absence of the solvent.

$$CaO + SO_3 \longrightarrow CaSO_4$$

(*ii*) Substances like BF_3, $AlCl_3$, etc. are known to behave as acids but they do not have protons to donate.

3. Lewis concept of Acids and Bases

The Arrhenius and Lowry-Bronsted concept of acids and bases are limited to substances which contain protons. G.N. Lewis (1923) proposed a more general and broader concept of acids and bases. According to this concept,

an acid is a substance (molecule or ion) which can accept a pair of electrons while a base is a substance (molecule or ion) which can donate a pair of electrons.

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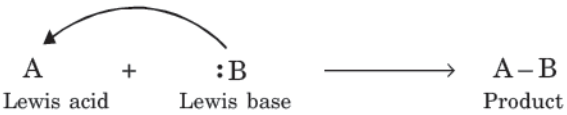


In other words, acids are electron pair *acceptors* while bases are electron pair *donors*. Thus, it is evident that any substance which has an unshared pair of electrons can act as a **Lewis base** while a substance which has an empty orbital that can accommodate a pair of electrons acts as **Lewis acid.** In fact, there is a donation of a pair of electrons from Lewis base to Lewis acid to form a coordinate bond between the two.

Lewis bases

According to Lewis concept, the following species can act as Lewis bases.

***(i)* Neutral species having at least one lone pair of electrons.** For example, ammonia, amines, alcohols, etc., act as Lewis bases because they contain a pair of electrons :

NH_3, $-NH_2$, R— O —H

***(ii)* Negatively charged species or anions.** For example, chloride, cyanide, hydroxide ions, etc. act as Lewis bases :

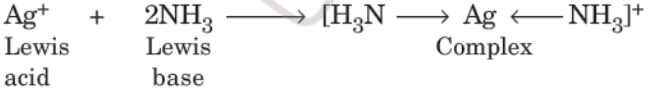
CN^-, Cl^-, OH^- etc.

Lewis acids

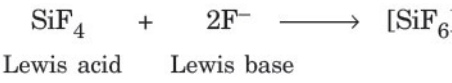
According to Lewis concept, the following species can act as Lewis acids :

***(i)* Molecules in which the central atom has incomplete octet.** For example, in BF_3, $AlCl_3$, $FeCl_3$, the central atom has only six electrons around it as shown below :

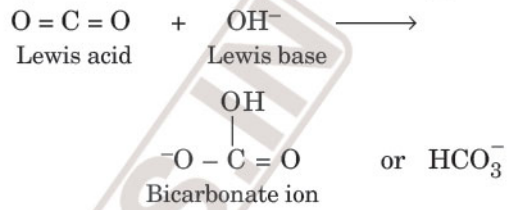
***(ii)* Simple cations can act as Lewis acids.** All cations are expected to act as Lewis acids since they are deficient in electrons. However, cations such as Na^+, K^+, Ca^{2+} ions, etc., have a very little tendency to accept electrons. While the cations like H^+, Ag^+ ion etc. have a greater electron accepting tendency and, therefore, act as Lewis acids.



***(iii)* Molecules in which the central atom has empty *d*-orbitals.** Due to the presence of empty *d*-orbitals, the central atoms in these molecules can expand their outer octets by accepting electrons from other substances (Lewis bases). The molecules such as SiF_4, $SnCl_4$, PF_5, etc. act as Lewis acids.



***(iv)* Molecules in which atoms of dissimilar electronegativities are joined by multiple bonds.** For example, CO_2 and SO_2 act as Lewis acids. The structure of CO_2 may be represented as O = C = O. Under the influence of the attacking Lewis base, one π-electron pair will be shifted towards the oxygen atom.



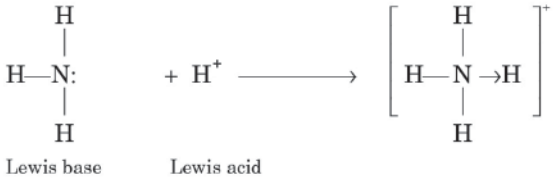
NOTE

It may be noted that **all Bronsted bases are also Lewis bases but all Bronsted acids are not Lewis acids.** According to Bronsted concept, a base is substance which can accept a proton. While according to Lewis, a base is a substance which can donate a pair of electrons. Lewis bases generally contain one or more lone pair of electrons and therefore, they can also accept a proton (Bronsted bases). Thus, **all Lewis bases are also Bronsted bases**. On the other hand, Bronsted acids are those which can give a proton (for example, HCl, H_2SO_4) but they are not capable of accepting a pair of electrons. Hence, **all Bronsted acids are not Lewis acids.**

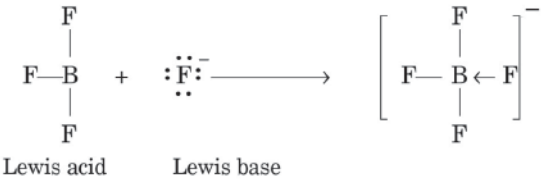
Acid-base reactions according to Lewis theory.

Some of the reactions involving the combination of Lewis acids and Lewis bases are :

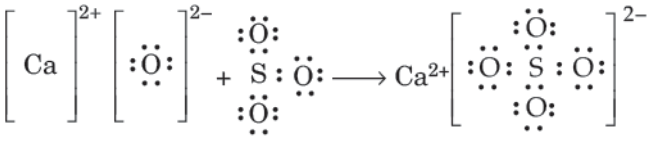
(*i*) *Combination between H^+ ion and NH_3*



(*ii*) *Combination between BF_3 and F^- ion*



(*iii*) *Combination between CaO and SO_3*



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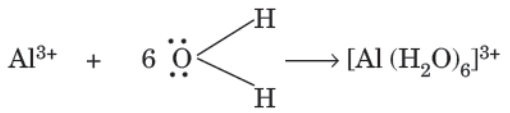
(*iv*) *Hydration of a metal ion.*



Limitations of Lewis Concept

Though Lewis concept of acids and bases is more general than Arrhenius as well as Bronsted-Lowry concepts, yet it has several drawbacks as discussed below :

(*i*) Lewis concept is too general and includes all the coordination compounds and coordination reactions. This, however, may not always be true.

(*ii*) It does not explain the behaviour of well known protonic acids like HCl, H_2SO_4, etc. which do not form coordinate bonds with bases. Therefore, these are not regarded as acids according to Lewis Concept.

(*iii*) It does not explain the relative strengths of acids and bases.

(*iv*) Acid-base reactions are usually fast but the formation of coordination compounds is slow. Hence, it does not fit in the acid-base reaction concept.

(*v*) The catalytic activity of many acids is due to H^+ (*aq*) ion. Since a Lewis acid need not contain hydrogen, therefore, many Lewis acids will not possess catalytic property.

SOLVED EXAMPLES

Example 38.

(*a*) *What are conjugate bases of each of the following :*

HS^-, H_3O^+, $H_2PO_4^-$, HSO_4^-, CH_3COOH, $[Al(H_2O)_6]^{3+}$, H_2SO_4

(*b*) *Give the conjugate acids of the following :*

OH^-, HCO_3^-, HPO_4^{2-}, CH_3NH_2 , CO_3^{2-}, CH_3COOH, NH_2^-, $HCOO^-$

(*c*) *Which of the following behave both as Bronsted acids as well as Bronsted bases ?*

H_2O, HCO_3^-, H_2SO_4, H_3PO_4, HS^-

Solution: (*a*) Conjugate bases :

HS^-	:	S^{2-}
H_3O^+	:	H_2O
$H_2PO_4^-$	:	HPO_4^{2-}
HSO_4^-	:	SO_4^{2-}
CH_3COOH	:	CH_3COO^-
$[Al(H_2O)_6]^{3+}$	:	$[Al(H_2O)_5OH]^{2+}$
H_2SO_4	:	HSO_4^-

(*b*) Conjugate acids

OH^-	:	H_2O
HCO_3^-	:	H_2CO_3
HPO_4^{2-}	:	$H_2PO_4^-$
CH_3NH_2	:	$CH_3NH_3^+$
CO_3^{2-}	:	HCO_3^-
CH_3COOH	:	$CH_3COOH_2^+$
NH_2^-	:	NH_3
$HCOO^-$	:	$HCOOH$

(*c*) H_2O, HCO_3^-, HS^- behave both as acids and bases. These are called *amphoteric substances.*

Important Tips

To write **conjugate acid, add** H^+

To write **conjugate base, subtract** H^+

Example 39.

(*a*) *Write the conjugate acids for the following Bronsted bases :*

NH_2^-, NH_3 and $HCOO^-$

(*b*) *Write the conjugate bases for the following Bronsted acids :*

HF, H_2SO_4, HCO_3^-. **N.C.E.R.T.**

Solution: (*a*) Conjugate acids :

(*i*)	NH_2^-	:	NH_3
(*ii*)	NH_3	:	NH_4^+
(*iii*)	$HCOO^-$	:	$HCOOH$

(*b*) Conjugate bases :

HF	:	F^-
H_2SO_4	:	HSO_4^-
HCO_3^-	:	CO_3^{2-}

Example 40.

The species H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acids and bases. Give the corresponding conjugate acid and base.

N.C.E.R.T.

Solution: The conjugate acids and bases are :

Species	Conjugate acid	Conjugate base
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

Example 41.

Classify the following species into Lewis acids and Lewis bases and show how these act as such :

(*a*) HO^- (*b*) F^-

(*c*) H^+ (*d*) BCl_3 **N.C.E.R.T.**

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Solution:

(*a*) HO^- is a Lewis base because it can donate a pair of electrons.

(*b*) F^- acts as a Lewis base because it can donate a pair of electrons.

(*c*) H^+ is a Lewis acid because it can accept a lone pair of electrons from bases like OH^- and F^- ions.

(*d*) BCl_3 acts as a Lewis acid because it is electron deficient and can accept a lone pair of electrons.

Practice Problems

51. Classify the following into acids and bases according to Lewis concept :

S^{2-}, H^+, OH^-, BF_3, Ni^{2+} , F^-

52. Which of the following can act both as a Bronsted acid and a Bronsted base ?

(*a*) HCO_3^- (*b*) O_2^- (*c*) NH_3 (*d*) H_2O (*e*) HS^-

53. Write the formula of the conjugate base of each of the following :

H_2O, HSO_4^-, NH_4^+, CH_3COOH, H_3PO_4, $CH_3NH_3^+$

54. Write the formula of conjugate acid of each of the following :

S^{2-}, CH_3NH_2, NH_2^-, NH_3, $H_2PO_4^-$

55. Write the conjugate acid or base for the following species :

$HClO_4$, OH^-, F^-, CO_3^{2-}, S^{2-}

56. Write the formula of conjugate acids of :

(*i*) C_6H_5OH (*ii*) NH_2NH_2 (*iii*) HCO_3^-

57. Classify the following as an acid, a base or amphoteric :

(*i*) HSO_4^- (*ii*) IO^- (*iii*) HI (*iv*) OH^-

58. Write the proton transfer equilibria for the following acids in aqueous solution and identify conjugate acid base pairs in each :

(*i*) HCN (*ii*) CH_3COOH

59. Which of the following are Lewis acids ?

(*i*) H_2O (*ii*) BF_3, (*iii*) H^+ (*iv*) NH_4^+ ***N.C.E.R.T.***

60. Write the conjugate acid/base for the following species :

HNO_2, CN^-, $HClO_4$, F^-, OH^-, CO_3^{2-} and S^{2-}.

N.C.E.R.T.

Answers to Practice Problems

51. Lewis acids are H^+, BF_3 , Ni^{2+}, others are Lewis bases.

52. (*a*), (*c*), (*d*), (*e*)

53. OH^-, SO_4^{2-}, NH_3, CH_3COO^-, $H_2PO_4^-$, CH_3NH_2

54. HS^-, $CH_3NH_3^+$, NH_3, NH_4^+, H_3PO_4

55. ClO_4^-, H_2O, O^{2-}, HF, HCO_3^-, HS^-

56. (*i*) $C_6H_5OH_2^+$ (*ii*) $NH_2NH_3^+$ (*iii*) H_2CO_3

57. (*i*) amphoteric (*ii*) base (*iii*) acid (*iv*) amphoteric

58. (*i*) HCN, CN^-; H_2O, H_3O^+
(*ii*) CH_3COOH, CH_3COO^-; H_2O, H_3O^+

59. BF_3, H^+ and NH^+_4

60. NO_2^-, HCN, ClO_4^-, HF, H_2O, HCO_3^-, HS^-.

IONISATION CONSTANT OF WATER AND IONIC PRODUCT OF WATER

Water is a weak electrolyte and undergoes self dissociation to a small extent as :

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The dissociation constant for the ionization of water is :

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Since the degree of dissociation of water is very small, the concentration of undissociated water may be practically taken as constant. Thus, we have

$$K \times [H_2O]^2 = [H_3O^+][OH^-]$$

or $$K \times \text{constant} = [H_3O^+][OH^-]$$

or $$K_w = [H_3O^+][OH^-]$$

where K_w is a constant and is known as **ionic product of water.** Its value is constant at a particular temperature and varies with the change in temperature. At 298 K, the value of K_w is 1.008×10^{-14} mol^2 L^{-2}. That is,

$K_w = [H_3O^+][OH^-] = 1.008 \times 10^{-14}$

or $= 1 \times 10^{-14}$ (for simplicity) at 298 K

It is quite evident that the concentrations of H_3O^+ and OH^- ions are equal in pure water so that

$$[H_3O^+] = OH^-$$

Now $K_w = [H_3O^+][OH^-] = 1.008 \times 10^{-14}$ mol^2 L^{-2}

or $[H_3O^+][OH^-] = 1.008 \times 10^{-14}$

or $[H_3O^+]^2 = 1.008 \times 10^{-14}$

or $[H_3O^+] = \sqrt{1.008 \times 10^{-14}}$

$= 1.0 \times 10^{-7}$ mol L^{-1}

Thus, in pure water, $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ mol L^{-1} at 298 K

The density of pure water is 1000 g/L and its molar mass is 18.0 g mol^{-1}. Therefore, the molarity of pure water can be given as :

$$[H_2O] = \frac{1000\ g/L}{18.0\ g\ mol^{-1}} = 55.55\ M$$

Thus, the ratio of dissociated water to that of undissociated water is $\frac{1 \times 10^{-7}}{55.55} = 1.8 \times 10^{-9}$ or approx 2×10^{-9}. Thus, equilibrium lies mainly towards undissociated water.

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Effect of Temperature on K_w

The values of $[H_3O^+]$ and $[OH^-]$ are always equal at all temperatures but values of K_w are different at different temperatures. The values of K_w at different temperatures are given in Table 4.

Table 4. Ionic product of water at different temperatures.

Temperature (K)	K_w (mol^2 L^{-2})
273	0.113×10^{-14}
283	0.292×10^{-14}
295	1.00×10^{-14}
298	1.008×10^{-14}
323	5.474×10^{-14}
373	7.50×10^{-14}

It is clear that **the value of K_w increases with rise in temperature.** This can be easily understood as follows :

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad \Delta H = +57.3 \text{ kJ}$$

In accordance with Le-Chatelier's principle, increase in temperature will shift the equilibrium in the forward direction producing larger concentrations of H_3O^+ and OH^- ions. Hence, K_w increases with rise in temperature.

Hydrogen and Hydroxyl Ion Concentration in Aqueous Solutions of Acids and Bases

The ionic product is very important quantity in aqueous solutions because it controls the relative concentrations of H^+ and OH^- ions because their product is constant. In pure water, the concentrations of H_3O^+ ions and OH^- ions are equal. But when an acid such as HCl or a base such as NaOH is added to the neutral solution, then concentrations of H_3O^+ and OH^- change and do not remain equal. However, the value of ionic product of water, K_w at a particular temperature always remains constant irrespective of the fact whether water is pure or some acid or a base has been added to it.

***(i)* Change in H_3O^+ and OH^- ions concentration on the addition of an acid.** If we add a few drops of acid (say HCl) to water, the concentration of H_3O^+ ions becomes large (more than 10^{-7} mol L^{-1}). Consequently, the dissociation equilibrium of water shifts in the reverse direction (Le-Chatelier's principle) *i.e.*, H_3O^+ ions would combine with OH^- ions to form undissociated water molecules so that the value of K_w in the solution may remain the same as that in water. The concentration of OH^- ions may be calculated as :

$$[OH^-] = \frac{K_w}{[H_3O^+]}$$

Thus, **the concentration of H_3O^+ ions will be more than the concentration of OH^- ions in acidic solution.**

***(ii)* Change in H_3O^+ and OH^- ions concentration on the addition of a base.** If we add a few drops of base (say NaOH) to water, the concentration of OH^- increases but the concentration of hydrogen ion decreases. The concentration of $[H_3O^+]$ can be calculated as :

$$[H_3O^+] = \frac{K_w}{[OH^-]}$$

Thus, **in basic solution, the H_3O^+ concentration will be less than OH^- ions concentration.**

Thus it may be concluded that hydronium and hydroxyl ions are always present in the solution whether it is acidic or basic. However, their concentrations in the two cases differ.

In acidic solution : $[H_3O^+] > [OH^-]$
In basic solution : $[H_3O^+] < [OH^-]$
In neutral solution : $[H_3O^+] = [OH^-]$

EXPRESSING HYDROGEN ION CONCENTRATION–pH SCALE

We have learnt that pure water contains equal concentration of hydronium and hydroxyl ions and the concentrations are :

$$[H_3O^+] = [OH^-] = 1 \times 10^{-7} \text{ mol } L^{-1} \text{ at } 298 \text{ K}$$

If the concentration of H_3O^+ ions is greater than 1×10^{-7} mol L^{-1}, then the solution is acidic while for basic solution the concentration of H_3O^+ ions is less than 1×10^{-7} mol L^{-1}. In other words, the concentration of hydrogen ions gives an idea about the acidic and basic nature of the aqueous solution. Sorensen in 1909, suggested a new term for expressing the concentration of hydrogen ions known as **pH** or **pH scale.*** The **pH of a solution** is defined as

the negative logarithm of the H_3O^+ ion concentration in moles per litre.

Mathematically, it may be expressed as :

$$pH = -\log [H_3O^+] \text{ or } \log \frac{1}{[H_3O^+]}$$

For neutral solution at 298 K,

$[H_3O^+] = [OH^-] = 1 \times 10^{-7}$ mol L^{-1} so that

$pH = -\log [H_3O^+] = -\log (1.0 \times 10^{-7}) = 7$

In a similar way, by substituting different values of $[H_3O^+]$ in the above relation, it can be seen that

For acidic solution **pH < 7**
For basic solution **pH > 7**
For neutral solution **pH = 7**

* The symbol pH is derived from the Danish word *Potenz* meaning *power*. Thus pH means *power of hydrogen ions.*

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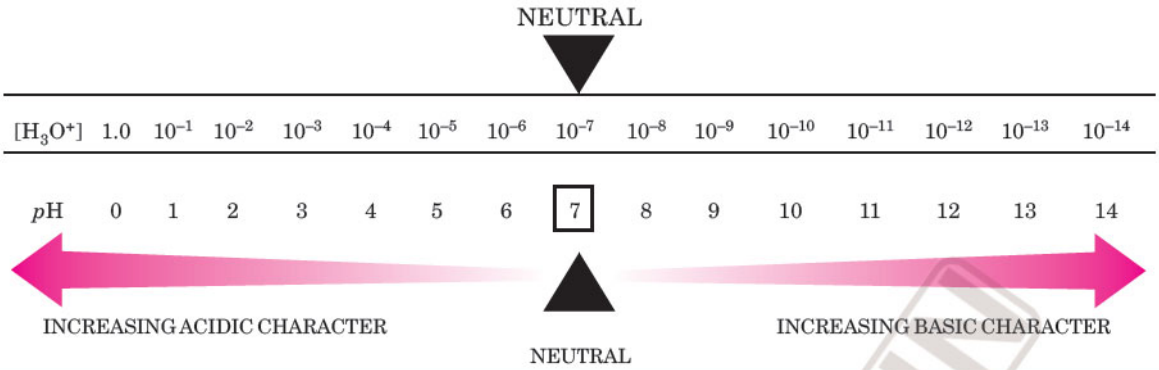

Fig. 18. pH scale.

It may be noted that pH is defined as the negative logarithm to base 10 of the activity of hydrogen ion, *i.e.* a_{H^+}. At low concentrations, the activity of hydrogen ion is numerically equal to its molarity represented as $[H^+]$.

It should be noted that activity of hydrogen ion does not have any units and can be defined as

$$a_{H^+} = [H^+]$$

where $[H^+]$ is in mol L^{-1}

Thus pH may be defined as :

$$pH = -\log (a_{H^+}) = -\log [H^+]$$

Hence a scale has been introduced to express the acidic and basic characters of a solution in terms of pH value (Fig. 18).

Like pH; it is also possible to define pOH as

$$pOH = -\log [OH^-]$$

But we know that

$$[H_3O^+][OH^-] = K_w$$

$$\log [H_3O^+][OH^-] = \log K_w$$

$$\log [H_3O^+] + \log [OH^-] = \log K_w$$

$$-pH - pOH = -pK_w$$

or $$pH + pOH = pK_w$$

$$\text{At } 25°C,\ pK_w = 14$$

$$\therefore \quad pH + pOH = 14$$

It may be noted that solutions having pH between 0 to 2 are **strongly acidic,** those with pH between 2 to 4 are **moderately acidic** while the others having pH between 4 to 7 are **weakly acidic.** Similarly, the solutions having pH value between 7 to 10 are **weakly basic,** those having pH 10 to 12 are **moderately basic** whereas the others which have pH range between 12 to 14 are **strongly basic.**

The pH of a solution can be roughly measured with a strip of universal indicator pH paper. This paper gives different colours at different pH values. Nowadays pH paper is available with four strips on it. The different strips have different colours at the same pH value (Fig. 19). The pH of a solution with the help of these papers can be determined with an accuracy of about 0.5.

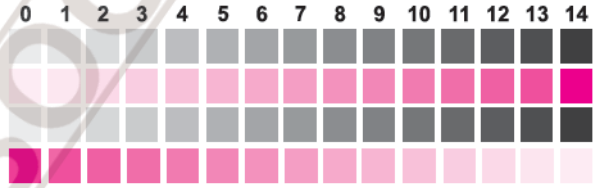

Fig. 19. pH-paper with four strips that may have different colours at the same pH.

For exact pH determination **indicators** are used. These are chemical substances which undergo pH-dependent colour changes as they are weak acids possessing different colours in their acid and conjugate base forms.

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

Indicator acid — Colour A

Conjugate acid

Conjugate base — Colour B

Such compounds are useful indicators in acid-base titrations and finding out H^+ ion concentration. Bromothymol blue and phenolphthalein are some common indicators.

However, more precise measurements, are made with a *p*H meter which reports the *p*H directly. pH meters of different size and accuracy are commercially available these days. These are commonly used in laboratories, factories and field work for measurement of pH of different solutions upto 0.001 precision.

The pH of some common substances are given in Table 5 ahead.

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Table 5. pH of some common substances

Substance	pH	Substance	pH
1 M NaOH solution	14	Beer	4.0 – 5.0
0.1 M NaOH solution	13		
1M NH_3 (household ammonia)	11.6	Black coffee	5.0
Lime water	10.5	Tomato juice	4.0 – 4.4
Milk of magnesia	10		
[saturated $Mg(OH)_2$]		Soft drinks	3.0
Egg white, sea water	7.8	Vinegar	2.4–3.4
Blood	7.3–7.5	Lemon juice	2.2–2.4
Saliva	6.5–7.5	Gastric juice	1.0–3.0
Urine	5.5–7.5	Battery acid	0.5
Milk	6.8	1 M HCl	≈ 0

SOLVED EXAMPLES

Example 42.

Calculate the pH of a sample of soft drink whose hydronium ion concentration is 3.8×10^{-3} M.

N.C.E.R.T.

Solution:

$$[H_3O^+] = 3.8 \times 10^{-3}$$

$$pH = -\log [H_3O^+]$$

$$= -\log (3.8 \times 10^{-3})$$

$$= -(\log 3.8 - 3 \log 10)$$

$$= -\log 3.8 + 3.0 \quad (\because \log 3.8 = 0.589)$$

$$= -0.58 + 3.0$$

$$= \mathbf{2.42}$$

Example 43.

The pH of a tomato juice is 4.4. Calculate $[H_3O^+]$ and $[OH^-]$.

Solution:

$$pH = -\log [H_3O^+]$$

or $$-\log [H_3O^+] = 4.4$$

or $$\log [H_3O^+] = -4.4$$

$$= -4 - 1 + 1 - 0.4$$

$$= -5 + 0.6$$

Taking antilog,

$$\therefore [H_3O^+] = 3.98 \times 10^{-5} \text{ mol } L^{-1}$$

Now, $$K_w = [H_3O^+][OH^-]$$

or $$[OH^-] = \frac{K_w}{[H_3O^+]}$$

$$= \frac{1 \times 10^{-14}}{3.98 \times 10^{-5}} = 2.5 \times 10^{-10} \text{ mol } L^{-1}$$

Thus, $\mathbf{[H_3O^+] = 3.98 \times 10^{-5} \text{ mol } L^{-1}}$,

$\mathbf{[OH^-] = 2.5 \times 10^{-10} \text{ mol } L^{-1}}$

Example 44.

The value of K_w is 9.55×10^{-14} at a certain temperature. Calculate the pH of water at this temperature.

Solution:

$$K_w = 9.55 \times 10^{-14}$$

For water $[H_3O^+] = [OH^-]$ and

$$K_w = [H_3O^+][OH^-] = 9.55 \times 10^{-14}$$

or $$[H_3O^+][H_3O^+] = 9.55 \times 10^{-14}$$

$$[H_3O^+] = \sqrt{9.55 \times 10^{-14}} = 3.09 \times 10^{-7} \text{ M}$$

$$pH = -\log (3.09 \times 10^{-7})$$

$$= -(\log 3.09 + \log 10^{-7})$$

$$= -(0.49 - 7) = \mathbf{6.51}$$

Example 45.

Calculate the hydronium ion concentration of each of the following solutions whose pH values are :

(i) 7.52 (ii) 0.00 (iii) 2.50

Solution: $pH = -\log [H_3O^+]$

or $$\log [H_3O^+] = -pH$$

(i) $$\log [H_3O^+] = -7.52$$

$$= -7 - 1 + 1 - 0.52$$

$$= \bar{8}.48$$

Taking anitlog

$$[H_3O^+] = \mathbf{3.10 \times 10^{-8} \text{ mol } L^{-1}}$$

(ii) $$\log [H_3O^+] = 0.00$$

Taking antilog

$$[H_3O^+] = \mathbf{1}$$

(iii) $$\log[H_3O^+] = -2.50$$

$$= -2 - 1 + 1 - 0.50$$

$$= \bar{3}.50$$

Taking antilog

$$\therefore [H_3O^+] = \mathbf{3.16 \times 10^{-3} \text{ mol}^{-1}}$$

Practice Problems

61. Calculate $[H_3O^+]$ and $[OH^-]$ for blood serum, the pH of which is 7.4.

62. The pH of a solution of lemon juice at 298 K is 2.32. Calculate $[H_3O^+]$ and $[OH^-]$ in its solution.

63. The pH of a sample of vinegar is 3.76. Calculate the concentration of H^+ ions in it. **N.C.E.R.T.**

64. Calculate the H_3O^+ ions concentration of the following biological fluids whose *p*H are given below :

(i) Human blood = 7.38

(ii) Human saliva = 6.4

(iii) Human stomach fluid = 1.2

(iv) Human muscle fluid = 6.83 **N.C.E.R.T.**

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65. The pH of stomach fluids is about 1.7. Calculate the H_3O^+ concentration.

Answers to Practice Problems

61. $[H_3O^+] = 3.98 \times 10^{-8}$, $[OH^-] = 2.5 \times 10^{-7}$

62. 4.8×10^{-3}, 2.08×10^{-12} mol L^{-1}

63. 1.73×10^{-4} M

64. (*i*) 4.17×10^{-8} M
(*ii*) 3.98×10^{-7} M
(*iii*) 6.3×10^{-2} M
(*iv*) 1.48×10^{-7} M

65. 2×10^{-2} mol L^{-1}

Hints & Solutions on page 94

ACID-BASE EQUILIBRIA AND IONIZATION OF ACIDS AND BASES

Most of the chemical and biological reactions take place in aqueous medium and therefore, it is useful to understand the ionization of acids and bases. Different acids and bases dissociate to different extents in aqueous solutions. The strength of an acid or a base is experimentally measured by determining its dissociation or ionisation constant.

Dissociation or Ionisation Constants of Acids in Water

Strong acids dissociate almost completely in water and therefore, the molar concentration of H^+ ions in the solution is same as that of acid itself. For example, a 0.1 M solution of strong acid, HCl is completely dissociated to give a solution which contains 0.1 M each of H^+ and Cl^- ions. Some common strong acids are :

HBr (*aq*), HI (*aq*), HNO_3 (*aq*), $HClO_4$ (*aq*), $ClSO_3H$ (*aq*), FSO_3H (*aq*), $HSbF_6$, H_2SO_4 (*aq*), etc.

Similarly, a strong base like NaOH is also completely ionised in solution to give Na^+ and OH^- ions. Other common strong bases are KOH (aq), RbOH (aq), CsOH(*aq*), $Ba(OH)_2$, $Ca(OH)_2$, etc. Most of the acids and bases are weak and are partially ionized in aqueous solutions. The relative strengths of weak acids can be compared in terms of their dissociation or ionisation constants. For example, the dissociation equilibrium of an acid HA may be represented as :

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

Applying law of chemical equilibrium,

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

Since water is present in a large quantity, its concentration remains practically constant. The concentration of water may be combined with K to give another constant K_a *i.e.*, $K \times [H_2O] = K_a$.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

($[H_2O]$ remains constant)

K_a is called **dissociation** or **ionisation constant** of an acid. **The larger the value of K_a, higher is the concentration of H_3O^+ and therefore, stronger is the acid.** Knowing the dissociation constants of acids, their relative strengths can be compared. For example, consider the following examples :

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.80 \times 10^{-5}$$

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]} = 4.0 \times 10^{-7}$$

Since K_a for CH_3COOH is larger than K_a for HCN, acetic acid is a stronger acid than HCN.

Concentration of H^+ ions for Weak Acids

The ionisation constant can be used to calculate the degree of dissociation or ionisation and the concentration of H^+ ions.

Degree of **dissociation or ionisation** may be defined as

the fraction of the total number of molecules of an electrolyte (acid or base) which ionises into ions.

It is generally denoted by the symbol α (alpha). Thus,

Degree of ionisation,

$$\alpha = \frac{\text{Number of molecules of the electrolyte which ionise}}{\text{Total number of molecules of the electrolyte}}$$

If c is the number of moles of the acid in one litre of the solution and α is the degree of ionisation, then the concentrations of each species at equilibrium are :

	HA	+	H_2O	$\rightleftharpoons$	H_3O^+	+	A^-
Initial conc.	c				0		0
Equilibrium conc.	$c(1-\alpha)$				$c\alpha$		$c\alpha$

$$[HA] = c(1-\alpha), [H_3O^+] = c\alpha, [A^-] = c\alpha$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(c\alpha)\times(c\alpha)}{c(1-\alpha)}$$

$$= \frac{c\alpha^2}{1-\alpha}$$

For weak acids, α is very small so that $1 - \alpha \approx 1$.

$$\therefore \quad K_a = c\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{c}}$$

$$\therefore \quad [H_3O^+] = c\alpha = c\sqrt{\frac{K_a}{c}} = \sqrt{K_a c}$$

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The values of ionization constants of some selected acids are given in Table 6.

Table 6. Ionization constants of some weak acids

Acid	Ionization constant K_a
Sulphurous acid, H_2SO_3	1.5×10^{-2}
Chlorous acid, $HClO_2$	1.0×10^{-2}
Hydrofluoric acid, HF	3.5×10^{-4}
Nitrous acid, HNO_2	4.5×10^{-4}
Formic acid, HCOOH	1.8×10^{-4}
Niacin, C_5H_4NCOOH	1.5×10^{-5}
Benzoic acid, C_6H_5COOH	6.5×10^{-5}
Acetic acid, CH_3COOH	1.74×10^{-5}
Carbonic acid, H_2CO_3	4.3×10^{-7}
Hypochlorous acid, HClO	3.0×10^{-8}
Hypobromous acid, HBrO	2.0×10^{-9}
Boric acid, H_3BO_3	7.2×10^{-10}
Hydrocyanic acid, HCN	4.9×10^{-10}
Phenol, C_6H_5OH	1.3×10^{-10}
Hydroiodous acid, HIO	2.3×10^{-11}

The pH scale for hydrogen ion concentration had been useful and it has been extended to other species and quantities. We may also write :

$$pK_a = -\log K_a$$

This means **that stronger acid will have higher K_a value but smaller pK_a value while a weaker acid will have small K_a value but higher pK_a value. In other words.**

Larger the value of pK_a, weaker the acid is.

Knowing the value of ionization constant, K_a of an acid and its initial concentrations, it is possible to calculate the equilibrium concentrations of all species and degree of ionization of the acid and the pH of the solution. From the value of H_3O^+ ions calculated above, pH can be calculated as :

$$[H_3O^+] = \sqrt{K_a c}$$

and $$pH = -\log [H_3O^+]$$

Dissociation or Ionisation Constants of Bases in Water

In a similar way, the ionisation constant of a base BOH in water may be represented as :

$$BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$$

$\therefore$ The ionisation constant of the base, K_b,

$$\therefore \quad K_b = \frac{[B^+][OH^-]}{[BOH]}$$

(Concentration of water remains constant)

If c is the number of moles of the base in one litre of the solution and α is the degree of ionisation, then the concentrations of each species at equilibrium are :

$$[B^+] = c\alpha,\ [OH^-] = c\alpha,\ [BOH] = c(1-\alpha)$$

$$\therefore \quad K_b = \frac{(c\alpha)\times(c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

But for weak bases, α is very small so that $1-\alpha \approx 1$

$$\therefore \quad K_b = c\alpha^2 \qquad \text{or} \quad \alpha = \sqrt{\frac{K_b}{c}}$$

and $$[OH^-] = c \times \sqrt{\frac{K_b}{c}} = \sqrt{K_b . c}$$

From this, H_3O^+ conentration and pH can be calculated as :

$$H_3O^+ = \frac{K_w}{[OH^-]}$$

and $$pH = -\log [H_3O^+]$$

Like pK_a, we can define

$$pK_b = -\log K_b$$

This means that **strong base will have higher K_b value but smaller pK_b value while a weaker base will have smaller K_b value but higher pK_b value. In other words.**

Larger the value of pK_b, weaker the base is

The values of ionization constants of some selected bases are given in Table 7.

Table 7. Ionization constants of some weak bases

Base	Ionization constant K_b
Urea, $CO(NH_2)_2$	1.3×10^{-14}
Aniline, $C_6H_5NH_2$	4.3×10^{-10}
Pyridine, C_5H_5N	1.77×10^{-9}
Triethylamine $(C_2H_5)_3N$	6.45×10^{-5}
Hydroxylamine, NH_2OH	1.1×10^{-8}
Hydrazine, NH_2NH_2	1.7×10^{-6}
Ammonia, NH_3	1.8×10^{-5}
Trimethylamine, $(CH_3)_3$ N	6.5×10^{-5}
Quinine (plant product)	1.10×10^{-6}
Methylamine, CH_3NH_2	5.4×10^{-4}
Dimethylamine, $(CH_3)_2NH$	3.6×10^{-4}
Ethylamine, $C_2H_5NH_2$	6.5×10^{-4}

Calculation of pH or pOH of weak electrolytes

In general, the following stepwise approach is followed for calculating pH or pOH of weak electrolytes (acids or bases).

Step 1. Write the primary reaction for equilibrium expression.

If more than one reactions are occurring, then write balanced equation for all possible reactions *i.e.*,

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with species acting both as acid as well as base. The reaction with higher value of K_a or K_b is identified as primary reaction while the other is a subsidiary reaction. For example, in the ionization of HF in and water, the following reactions occur ;

(*i*) $HF + H_2O \rightleftharpoons H_3O^+ + F^-$ $K_a = 3.2 \times 10^{-4}$

(*ii*) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ $K_a = 1.0 \times 10^{-14}$

Since $K_a >> K_w$, the first reaction is the primary reaction.

Step 2. Write in a tabular form the following values for each of the species in the reaction :

(*i*) Initial concentration c

(*ii*) Change in concentration as proceeding to equilibrium in terms of degree of ionization, α.

(*iii*) Equilibrium concentrations. For simplicity sometimes the equilibrium concentrations are directly written without step (*ii*)

Step 3. Substitute equilibrium concentrations into equilibrium constant equation for the reaction and solve for α.

Step 4. Calculate the concentration of species present.

Step 5. Calculate pH as $pH = -\log [H_3O^+]$

Strengths of acids and bases can be compared on the basis of their dissociation constants. The acid (or a base) having a higher value of dissociation constant is stronger. But, for quantitative comparison, the concentration of H^+ ions should be determined for both acids in solution of equal molarity. In general, strength of two acids HA(1) and HA(2),

$$\frac{\text{Strength of acid HA(1)}}{\text{Strength of acid HA(2)}} = \sqrt{\frac{K_a(1)}{K_a(2)}}$$

of same concentration

where $K_a(1)$ and $K_a(2)$ are dissociation constants. Similarly, for two bases,

$$\frac{\text{Strength of base BOH(1)}}{\text{Strength of base BOH(2)}} = \sqrt{\frac{K_b(1)}{K_b(2)}}$$

SOLVED EXAMPLES

Type A: Calculation of $[H^+]$ and $[OH^-]$ of strong electrolytes

Example 46.

Calculate the hydronium and hydroxyl ion concentrations in

(i) 0.01 M HCl

(ii) 0.005 M NaOH solution at 298 K.

Solution: (*i*) HCl completely ionises as :

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

Therefore, the concentration of hydronium ions is equal to that of hydrochloric acid,

i.e., $[H_3O^+] = [HCl]$

Here $[HCl] = 0.01\ M = 1 \times 10^{-2}\ M$

$\therefore$ $[H_3O^+] = 1 \times 10^{-2}\ M = \mathbf{1 \times 10^{-2}\ mol\ L^{-1}}$

Now, the ionic product, $K_w = [H_3O^+]\,[OH^-]$

or $$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1 \times 10^{-14}}{1 \times 10^{-2}} = \mathbf{1 \times 10^{-12}\ mol\ L^{-1}}$$

Thus $[H_3O^+] = \mathbf{1 \times 10^{-2}\ mol\ L^{-1}}$ and $[OH^-] = \mathbf{1 \times 10^{-12}\ mol\ L^{-1}}$

(*ii*) NaOH completely ionises as :

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

The concentration of OH^- ions is equal to that of the sodium hydroxide, *i.e.*

$[NaOH] = [OH^-]$

Here, $[NaOH] = 0.005\ M = 5 \times 10^{-3}\ mol\ L^{-1}$

$\therefore$ $[OH^-] = \mathbf{5 \times 10^{-3}\ mol\ L^{-1}}$

Now, $K_w = [H_3O^+]\,[OH^-]$

or $$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{5 \times 10^{-3}}$$

$= \mathbf{2 \times 10^{-12}\ mol\ L^{-1}}$

Thus, $[OH^-] = \mathbf{5 \times 10^{-3}\ mol\ L^{-1}}$ and

$[H_3O^+] = \mathbf{2 \times 10^{-12}\ mol\ L^{-1}}$

Practice Problems

66. Calculate the hydrogen ion and hydroxyl ion concentrations of solution containing 0.063 g of pure nitric acid per litre.

67. Calculate the $[H_3O^+]$ and $[OH^-]$ of

(*i*) 0.01 M NaOH (*ii*) 0.1 M HNO_3

68. Calculate the concentration of H_3O^+ ions in 0.001 M solution of $Ba(OH)_2$ assuming complete dissociation of $Ba(OH)_2$.

Answers to Practice Problems

66. $[H_3O^+] = 1 \times 10^{-3}\ mol\ L^{-1}$, $[OH^-] = 1 \times 10^{-11}\ mol\ L^{-1}$

67. (*i*) 1×10^{-12}, 1×10^{-2} (*ii*) 0.1, 1×10^{-13}

68. 5.0×10^{-12}

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Type B : Calculation of H^+ and OH^- concentration from ionization constant of weak acids and bases.

Example 47.

Calculate the concentration of hydroxyl ion in 0.1 M solution of ammonium hydroxide having $K_b = 1.8 \times 10^{-5}$.

Solution: $NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

Now $[NH_4^+] = [OH^-], [NH_4OH] = 0.1$ M

so that $$K_b = \frac{[OH^-]^2}{[NH_4OH]}$$

Substituting the values,

$$1.8 \times 10^{-5} = \frac{[OH^-]^2}{0.1}$$

or $$[OH^-]^2 = 1.8 \times 10^{-5} \times 0.1 = 1.8 \times 10^{-6}$$

or $$[OH^-] = (1.8 \times 10^{-6})^{1/2} = 1.34 \times 10^{-3}$$

Thus, concentration of OH^- ions = **1.34×10^{-3} mol L^{-1}.**

Example 48.

Calculate the per cent ionisation of 0.20 M solution of hydrocyanic acid, HCN. K_a for HCN $= 4.9 \times 10^{-10}$.

Solution:

	HCN	$\rightleftharpoons$	H^+	+	CN^-
Initial conc.	0.2		0		0
Equilibrium. conc.	0.2 (1 – α)		0.2α		0.2α

Let α is the degree of ionisation of HCN.

$$K_a = \frac{[H^+][CN^-]}{[HCN]}$$

$$4.9 \times 10^{-10} = \frac{(0.2\alpha)(0.2\alpha)}{0.2(1-\alpha)}$$

$$4.9 \times 10^{-10} = 0.2\,\alpha^2 \qquad (\because 1 - \alpha \approx 1)$$

$$\therefore \quad \alpha = \sqrt{\frac{4.9 \times 10^{-10}}{0.2}} = 4.95 \times 10^{-5}$$

$\therefore$ Per cent ionisation = **0.00495%**

Example 49.

At 298 K, a 0.1 M solution of acetic acid is 1.34% ionised. What is the ionisation constant K_a of acetic acid ?

Solution: Degree of ionisation, α = 1.34% = 0.0134

Concentration at equilibrium

$$CH_3COOH\,(aq) + H_2O \rightleftharpoons CH_3COO^-\,(aq) + H_3O^+$$

Since the initial concentration is 0.1 M, the number of moles of acetic acid ionised

$$= 0.1 \times 0.0134 = 0.00134 \text{ mol}$$

Number of moles of acetic acid unionised $= 0.1 - 0.00134 = 0.09866$ mol

According to the reaction, 1 mol of acetic acid gives 1 mol of CH_3COO^- and 1 mol of H_3O^+ ions. Therefore, 0.00134 mol of CH_3COOH will give 0.00134 mol of CH_3COO^- and 0.00134 mol of H_3O^+ ions. Thus, the concentrations at equilibrium are :

$$CH_3COOH\,(aq) + H_2O \rightleftharpoons CH_3COO^-\,(aq) + H_3O^+$$

0.09866 mol 0.00134 mol 0.00134 mol

$$K_a = \frac{[CH_3COO^-(aq)]\,[H_3O^+(aq)]}{[CH_3COOH(aq)]}$$

$$= \frac{(0.00134) \times (0.00134)}{0.09866} = \mathbf{1.82 \times 10^{-5}}$$

Example 50.

Calculate the concentration of H_3O^+ ions in a mixture of 0.02 M acetic acid and 0.1 M sodium acetate. K_a for acetic acid is 1.8×10^{-5}.

Solution: CH_3COOH (weak acid) ionises partially and sodium acetate (strong electrolyte) ionises completely in the solution. Let x be the number of moles of acetic acid ionized.

Then, the concentrations of various species are :

$$CH_3COOH(aq) + H_2O \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$CH_3COONa(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$$

Concentration of acetate ions from acetic acid = x

Since sodium acetate is completely ionised, the concentration of acetate ion from sodium acetate

$$= 0.1 \text{ M}$$

$\therefore$ Total $[CH_3COO^-] = 0.1 + x$

Concentration of acetic acid left unionized = $0.02 - x$

Now, x is very small in comparison to 0.1 so that

$[CH_3COO^-] = 0.1 + x \approx 0.1$ mol L^{-1}

$[CH_3COOH] = 0.02 - x \approx 0.02$ mol L^{-1}

Ionisation constant, K_a is :

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

or $$1.8 \times 10^{-5} = \frac{[H_3O^+] \times 0.1}{0.02}$$

or $$[H_3O^+] = \frac{1.8 \times 10^{-5} \times 0.02}{0.1} = \mathbf{3.6 \times 10^{-6}\ mol\ L^{-1}}$$

Practice Problems

69. Calculate the concentration of H^+ ions in 0.2 M solution of CH_3COOH. K_a for $CH_3COOH = 1.8 \times 10^{-5}$.

70. Calculate the H^+ ion concentration in 0.1 M CH_3COOH if the degree of dissociation of the acid is 0.0132.

Answers to Practice Problems

69. 1.897×10^{-3} M

70. 1.32×10^{-3} M

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Type C : Calculation of pH for strong electrolytes

Example 51.

Calculate the pH value of

(i) 0.001 M HNO_3 (ii) 0.01 M NaOH

Solution: (*i*) Since HNO_3 is a strong acid, it completely ionises and therefore, H_3O^+ ions concentration is equal to that of the acid itself *i.e.,*

$$[H_3O^+] = [HNO_3] = 0.001\ M = 1 \times 10^{-3}\ M$$

Now, $pH = -\log [H_3O^+]$

or $pH = -\log [1 \times 10^{-3}]$

$= -(-3) \log 10 = 3 \quad (\because \log 10 = 1)$

(*ii*) Since NaOH is a strong base, it completely ionises. Therefore, the hydroxyl ion concentration is equal to that of the base itself, *i.e.* $[OH^-] = [NaOH] = 0.01$

$$M = 1 \times 10^{-2} M$$

Now, $K_w = [H_3O^+]\,[OH^-]$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{1 \times 10^{-2}} = 1 \times 10^{-12}$$

$$pH = -\log [H_3O^+]$$

$$= -\log [1 \times 10^{-12}] = \mathbf{12}$$

Example 52.

The solubility of $Sr(OH)_2$ at 298 K is 19.32 g L^{-1} of solution. Calculate the concentration of strontium and hydroxyl ions and the pH of the solution. **N.C.E.R.T.**

Solution:

Molar mass of $Sr(OH)_2 = 87.6 + 2 \times 17 = 121.6$

$$\text{Solubilty} = \frac{19.23}{121.6}$$

$$= 0.1581\ M$$

$Sr(OH)_2$ ionizes as :

$$Sr(OH)_2 = Sr^{2+} + 2OH^-$$

$$[Sr^{2+}] = 0.1581\ M,$$

$$[OH^-] = 2 \times 0.1581 = 0.3162\ M$$

Now, $[H_3O^+]\,[OH^-] = K_w$

$$[H_3O^+] = \frac{1 \times 10^{-14}}{[OH^-]}$$

$$= \frac{1 \times 10^{-14}}{0.3162} = 3.163 \times 10^{-14}$$

$$pH = -\log [H_2O^+]$$

$$= -\log (3.163 \times 10^{-14})$$

$$= -(0.499 - 14)$$

$$= \mathbf{13.50.}$$

Example 53.

Assuming complete dissociation, calculate the pH of the following solutions :

(i) 0.003 M HCl *(ii) 0.002 M HBr*

(iii) 0.002 M KOH *(iv) 0.005 M NaOH*

Arrange these in the decreasing order of pH value and assuming complete dissociation :

Solution : (*i*) 0.003 M HCl **N.C.E.R.T.**

$$[H_3O^+] = [HCl] = 0.003\ M$$

$$pH = -\log [H_3O^+] = -\log (3.0 \times 10^{-3})$$

$$= -\log 3 + 3 = -0.477 + 3.0 = \mathbf{2.523}$$

(*ii*) 0.002 M HBr

$$[H_3O^+] = [HBr] = 0.002\ M$$

$$pH = -\log (H_3O^+)$$

$$= -\log (0.002) = -\log (2.0 \times 10^{-3})$$

$$= -\log 2.0 + 3 = -0.3010 + 3 = \mathbf{2.699}$$

(*iii*) 0.002 M KOH

$$[OH^-] = [KOH] = 0.002 = 2 \times 10^{-3}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12}$$

$$pH = -\log [H_3O^+] = -\log (5 \times 10^{-12})$$

$$= -\log 5 + 12 = -0.699 + 12 = \mathbf{11.301}$$

(*iv*) 0.005 M NaOH

$$[OH^-] = [NaOH] = 0.005\ M = 5.0 \times 10^{-3}\ M$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{5.0 \times 10^{-3}} = 2.0 \times 10^{-12}$$

$$pH = -\log [H_3O^+] = -\log (2.0 \times 10^{-12})$$

$$= -\log 2 + 12 = -0.301 + 12 = \mathbf{11.699}$$

Decreasing order of pH :

0.005 M NaOH > 0.002 M KOH > 0.002 M HBr > 0.003 M HCl

Example 54.

Calculate the pH of the following solutions :

(i) 0.3 g of $Ca(OH)_2$ dissolved in water to form 500 mL solution.

(ii) 1 mL of 13.6 M HCl is diluted with water to give 1 L of solution

(iii) 2 g of TlOH dissolved in waer to give 2L of solution.

(iv) 0.3 g of NaOH dissolved in water to give 200 mL of solution.

(atomic mass, Tl = 204, Ca = 40)

N.C.E.R.T.

Solution:

(*i*) 0.3 g of $Ca(OH)_2$ in 500 mL solution

$$\text{Concentration of solution} = \frac{0.3}{74} \times \frac{1000}{500}$$

(Molar mass of $Ca(OH)_2$ = 74u)

$$= 0.008\ M$$

Since $Ca(OH)_2$ is completely ionized :

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

$$\therefore [OH^-] = 2 \times 0.008 = 1.6 \times 10^{-2}\ M$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.6 \times 10^{-2}} = 6.25 \times 10^{-13}\ M$$

$$pH = -\log [H_3O^+] = -\log (6.25 \times 10^{-13})$$

$$= -\log 6.25 + 13 = -0.796 + 13 = \mathbf{12.204.}$$

(*ii*) 1 mL of 13.6 M HCl is diluted with water to give 1 L solution.

Molarity of the diluted solution :

$$M_1V_1 = M_2V_2$$

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$13.6\ M \times 1\ mL = M_2 \times 1000\ mL$

$\therefore \quad M_2 = \frac{13.6}{1000} = 1.36 \times 10^{-2}\ M$

$[H_3O^+] = 1.36 \times 10^{-2}\ M$

$pH = -\log [H_3O^+] = -\log (1.36 \times 0^{-2})$

$= -\log 1.36 + 2 = -0.134 + 2 = \mathbf{1.866}$

(*iii*) 2 g TlOH dissolved in 2 L of solution

Molar mass of TlOH = 204 + 16 + 1 = 221 *u*

$$\text{Conc. of solution} = \frac{2 \times 1}{221 \times 2}$$

$$= 4.52 \times 10^{-3}\ M$$

Since TlOH dissociates completely as

$$TlOH \rightleftharpoons Tl^+ + OH^-$$

$\therefore \quad [OH^-] = 4.52 \times 10^{-3}\ M$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{4.52 \times 10^{-3}} = 2.212 \times 10^{-12}\ M$$

$pH = -\log [H_3O^+] = -\log (2.212 \times 10^{-12})$

$= -(0.345 - 12) = \mathbf{11.655.}$

(*iv*) 0.3 g of NaOH dissolved in 200 mL of solution

$$\text{Conc. of solution} = \frac{0.3}{40} \times \frac{1000}{200}$$

$= 0.0375\ M$

($\because$ Molar mass of NaOH = 40)

Since NaOH dissociates completely as :

$$NaOH \rightleftharpoons Na^+ + OH^-$$

$[OH^-] = 0.0375\ M$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{0.0375} = 2.67 \times 10^{-13}$$

$pH = -\log [H_3O^+] = -\log (2.67 \times 10^{-13})$

$= -(4.265 - 13) = \mathbf{12.57.}$

Type D : Calculation of pH of weak acids and bases.

❑ **Example 55.**

Calculate the pH of 0.01 M solution of CH_3COOH. K_a for CH_3COOH at 298 K is 1.8×10^{-5}.

Solution: The dissociation equilibrium of acetic acid is :

$$CH_3COOH(aq) + H_2O(l) = H_3O^+(aq) + CH_3COO^-(aq)$$

Applying law of chemical equilibrium, we get

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Since, $[H_3O^+] = [CH_3COO^-]$

$$K_a = \frac{[H_3O^+]^2}{[CH_3COOH]}$$

Now, $[CH_3COOH] = 0.01\ M = 1 \times 10^{-2}\ M$

Substituting the values in equation (*i*),

$$1.8 \times 10^{-5} = \frac{[H_3O^+]^2}{1 \times 10^{-2}}$$

or $\quad [H_3O^+]^2 = 1.8 \times 10^{-5} \times 1 \times 10^{-2}$

or $\quad [H_3O^+] = (1.8 \times 10^{-7})^{1/2} = (18 \times 10^{-8})^{1/2}$

$= 4.242 \times 10^{-4}\ mol\ L^{-1}$

$pH = -\log [H_3O^+]$

$pH = -[\log 4.242 \times 10^{-4}]$

$= -[\log 4.242 - 4 \log 10]$

$= [4 - \log 4.242]$

$= [4 - 0.6276] = \mathbf{3.37}$

❑ **Example 56.**

The degree of ionization of a 0.1 M bromo acetic acid solution is 0.132. Calculate the pH of solution and the pK_a of bromo acetic acid **N.C.E.R.T.**

Solution:

Degree of dissociation, $\alpha = 0.132$

Concentration of H_3O^+ ion,

$[H_3O^+] = c\,\alpha = 0.1 \times 0.132 = 0.0132\ M$

$pH = -\log [H_3O^+]$

$= -\log (0.0132)$

$= -(-1.88) = \mathbf{1.88.}$

The dissociation constant,

$$K_a = \frac{c\alpha^2}{1 - \alpha}$$

$$= \frac{0.1 \times (0.132)^2}{1 - 0.132} = \mathbf{2.01 \times 10^{-3}}$$

$pK_a = -\log K_a$

$= -\log (2.01 \times 10^{-3})$

$= -(-2.7) = \mathbf{2.7.}$

❑ **Example 57.**

The pH of a 0.1 M monobasic acid (HA) is 4.5. Calculate the concentration of the species H^+, A^- and HA at equilibrium. Also calculate the value of K_a and pK_a of the acid.

Solution: $pH = 4.5$

or $\quad -\log [H_3O^+] = 4.5$

or $\quad \log [H_3O^+] = -4.5$ or $\bar{5}.5$

$\therefore \quad [H_3O^+] = 3.16 \times 10^{-5}$

Let the acid, HA ionises as :

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$[H_3O^+] = [A^-] = 3.16 \times 10^{-5}\ M$

$[HA]_{equi} = 0.1 - 3.16 \times 10^{-5} \approx 0.1\ M$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

But $[H_3O^+] = [A^-]$

$$K_a = \frac{[H_3O^+]^2}{[HA]}$$

Here $[HA] = 0.1\ mol\ L^{-1}$, $[H_3O^+] = 3.16 \times 10^{-5}\ mol\ L^{-1}$

$$K_a = \frac{(3.16 \times 10^{-5})^2}{0.1} = 1.0 \times 10^{-8}$$

$\therefore \quad K_a = 1.0 \times 10^{-8}$

$pK_a = -\log (1.0 \times 10^{-8}) = \mathbf{8}$

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Example 58.

Calculate $[H_3O^+]$, $[OH^-]$ and pH of a 0.2 M solution of HCN ($K_a = 7.2 \times 10^{-10}$).

Solution: The acid ionises as :

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

The dissociation constant may be written as :

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]}$$

Now, $[H_3O^+] = [CN^-]$

$$K_a = \frac{[H_3O^+]^2}{[HCN]}$$

Here, $K_a = 7.2 \times 10^{-10}$, $[HCN] = 0.2$ M

$$\therefore \quad 7.2 \times 10^{-10} = \frac{[H_3O^+]^2}{0.2}$$

$$\text{or } [H_3O^+]^2 = 7.2 \times 10^{-10} \times 0.2 = 1.44 \times 10^{-10}$$

$$\text{or } [H_3O^+] = (1.44 \times 10^{-10})^{1/2} = 1.2 \times 10^{-5} \text{ mol L}^{-1}$$

$$\text{Now, } [OH^-] = \frac{1 \times 10^{-14}}{1.2 \times 10^{-5}} = 8.33 \times 10^{-10} \text{ mol L}^{-1}$$

$$pH = -\log [H_3O^+]$$
$$= -\log (1.2 \times 10^{-5})$$
$$= -(\log 1.2 - 5 \log 10)$$
$$= (5 - \log 1.2) = 5 - 0.08 = \mathbf{4.92}$$

Example 59.

The ionization constant of HF is 3.2×10^{-4}. Calculate the degree of dissociation of HF in its 0.02 M solution. Calculate the concentration of all species present (H_3O^+, F^- and HF) in the solution and its pH.

N.C.E.R.T.

Solution: If c is the initial concentration and α is the degree of ionization of HF then

	HF	+ H_2O	$\rightleftharpoons$	H_3O^+	+	F^-
Initial conc.	c			0		0
at equi,	c(1–α)			cα		cα

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

$$= \frac{(c\,\alpha) \times (c\,\alpha)}{c\,(1-\alpha)} = \frac{c\,\alpha^2}{1-\alpha}$$

Since α is very small, $1 - \alpha \approx 1$

$$K_a = c\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{3.2 \times 10^{-4}}{0.02}} = 0.126$$

Degree of ionization of HF = 0.126

Equilibrium concentrations can be calculated as :

$[H_3O^+] = c\alpha = 0.02 \times 0.126 = 2.52 \times 10^{-3}$ M

$[F^-] = c\alpha = 0.02 \times 0.126 = 2.52 \times 10^{-3}$ M

$[HF] = c(1-\alpha) = 0.02\,(1 - 0.126) = 1.748 \times 10^{-2}$ M

Now $pH = -\log [H_3O^+]$

$= -\log (2.52 \times 10^{-3}) = \mathbf{2.60}$.

Example 60.

The pH of a 0.01 M solution of an organic acid is 4.15. Calculate

(i) the concentration of the anion

(ii) ionization constant of the acid

(iii) pK_a

N.C.E.R.T.

Solution :

$$pH = 4.15$$
$$-\log [H_3O^+] = 4.15$$

$$\text{or } \log [H_3O^+] = -4.15 = \bar{5}.85$$

$$\therefore \quad [H_3O^+] = \text{antilog } (\bar{5}.85)$$
$$= 7.08 \times 10^{-5}$$

Now $[H_3O^+] = [A^-] = 7.08 \times 10^{-5}$ M

(*i*) Concentration of anion = 7.08×10^{-5} M

(*ii*) Ionization constant of acid

$$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Concentration of undissociated acid = 0.01 – 0.000071

= 0.009929

$$\therefore \quad K_a = \frac{\left(7.08 \times 10^{-5}\right) \times \left(7.08 \times 10^{-5}\right)}{0.009929}$$

$$= 5.05 \times 10^{-7}$$

(*iii*) $pK_a = -\log K_a$

$= -(5.05 \times 10^{-7}) = \mathbf{6.26}$

Example 61.

Calculate the pH of 0.08 M solution of hypochlorous acid (HClO). The ionization constant of the acid is 2.5×10^{-5}. Calculate the per cent dissociation of HOCl.

Solution :

$$HOCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-\,(aq)$$

If c is the initial concentration and α is the degree of dissociation, then

Initial conc.	c	0	0
At equi.	c(1–α)	cα	cα

$$K_a = \frac{[H_3O^+][ClO^-]}{[HOCl]}$$

$$= \frac{(c\alpha) \times (c\alpha)}{c(1-\alpha)} \approx c\alpha^2$$

$$2.5 \times 10^{-5} = 0.08\alpha^2$$

$$\text{or } \alpha = \left(\frac{2.5 \times 10^{-5}}{0.08}\right)^{\frac{1}{2}} = 1.77 \times 10^{-2}$$

$$\therefore \quad [H_3O^+] = c\alpha = 0.08 \times 1.77 \times 10^{-2}$$
$$= 1.41 \times 10^{-3}$$

$$pH = -\log [H_3O^+]$$
$$= -\log (1.41 \times 10^{-3}) = \mathbf{2.85}$$

$$\text{Per cent dissociation} = \frac{[HOCl]\text{dissociated}}{[HOCl]\text{undissociated}} \times 100$$

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$[HOCl]_{dissociation} = c\alpha = 0.08 \times 1.77 \times 10^{-2}$
$= 1.41 \times 10^{-3}$
$[HOCl]_{undissociated} = c(1-\alpha) \approx c = 0.08$

$\text{Per cent dissociation} = \frac{1.41\times10^{-3}}{0.08} \times 100$
$= \mathbf{1.76\%}$

Example 62.

The pH of 0.1 M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

N.C.E.R.T.

Solution :

HCNO ionizes as :

$$HCNO \rightleftharpoons H^+ + CNO^-$$

The dissociation constant

$$K_a = \frac{[H^+][CNO^-]}{[HCNO]}$$

$[H^+] = [CNO^-]$

Now $pH = 2.34$

$-\log [H^+] = 2.34$

$\log [H^+] = -2.34 = \bar{3}.66$

$[H^+] = \text{Anti log } (\bar{3}.66)$
$= 4.57 \times 10^{-3}$ M

$\therefore$ $[H^+] = [CNO^-] = 4.57 \times 10^{-3}$ M and $[HCNO] = 0.1$ M

$$K_a = \frac{(4.57\times10^{-3})\times(4.57\times10^{-3})}{0.1}$$
$$= \mathbf{2.09 \times 10^{-4}}$$

$\text{Degree of dissociation} = \alpha = \sqrt{\frac{K_a}{c}}$
$= \sqrt{\frac{2.09\times10^{-4}}{0.1}}$
$= 4.57 \times 10^{-2}$ or $= \mathbf{0.0457.}$

Example 63.

The pH of 0.004 M hydrazine solution is 9.7. Calculate its ionization constant K_b and pK_b.

N.C.E.R.T.

Solution : $NH_2NH_2 + H_2O \rightleftharpoons NH_2NH_3^+ + OH^-$

$$K_b = \frac{[NH_2NH_3^+][OH^-]}{[NH_2NH_2]}$$

Now $pH = 9.7$

$-\log [H_3O^+] = 9.7$

or $\log [H_3O^+] = -9.7$

or $= \bar{10}.3$

Taking antilog on both sides

$[H_3O^+] = 1.99 \times 10^{-10}$

$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1\times10^{-14}}{1.99\times10^{-10}}$

$= 5.025 \times 10^{-5}$

Now $[OH^-] = [NH_2NH_3^+] = 5.025 \times 10^{-5}$

$K_b = \frac{(5.025\times10^{-5})^2}{0.004} = 6.31 \times 10^{-7}$

$pK_b = -\log K_b = -\log 6.31 \times 10^{-7} = \mathbf{6.20}$

Type E : Calculation of pH of mixtures of acids and bases.

Example 64.

Calculate the pH of a solution formed by mixing equal volumes of two solutions A and B of a strong acid having pH = 6 and pH = 4 respectively.

Solution: pH of solution A = 6

$\therefore$ $[H_3O^+]$ of solution A $= 10^{-6}$ M

pH of solution B = 4

$\therefore$ $[H_3O^+]$ of solution B $= 10^{-4}$

On mixing one litre of each solution, total volume = 1 L + 1L = 2L

$[H_3O^+]$ in mixture $= \frac{10^{-4}+10^{-6}}{2}$

$= \frac{10^{-4}(1+0.01)}{2} = \frac{1.01\times10^{-4}}{2} = 5 \times 10^{-5}$

$pH = -\log (5 \times 10^{-5}) = \mathbf{4.3}$

Example 65.

Calculate the pH of the following solutions obtained by mixing:

(a) equal volumes of two solutions with pH = 4 and pH = 10.

(b) 400 mL of solution with pH = 3 and 100 mL of solution with pH = 4

(c) 200 mL of 0.1 M NaOH and 300 mL of 0.2 M KOH.

Solution: (a) For a solution having pH = 4,

$[H_3O^+] = 10^{-4}$ M

For a solution having pH = 10

$[H_3O^+] = 10^{-10}$ M

$\therefore$ $[OH^-] = \frac{10^{-14}}{10^{-10}} = 10^{-4}$ M

The two solutions will exactly neutralise each other and therefore, the resulting solution will be neutral and its pH will be 7.

(b) For a solution having pH = 3, $[H_3O^+] = 10^{-3}$ M

$\text{Conc. of } H_3O^+ \text{ in 400 mL} = \frac{10^{-3}}{1000} \times 400$

$= 4 \times 10^{-4}$ mol

For a solution having pH = 4, $[H_3O^+] = 10^{-4}$ M

$\text{Conc. of } H_3O^+ \text{ in 100 mL} = \frac{10^{-4}}{1000} \times 100$

$= 10^{-5}$ mol

Total H_3O^+ moles $= 4 \times 10^{-4} + 10^{-5}$
$= (4 + 0.1) \times 10^{-4}$
$= 4.1 \times 10^{-4}$ mol

Total volume = 400 + 100 = 500 mL

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$$[H_3O^+] = \frac{4.1\times10^{-4}}{500}\times1000$$

$$= 8.2 \times 10^{-4}\ M$$

$$\therefore \quad pH = -\log(8.2 \times 10^{-4})$$

$$= 4 - 0.9138 = \mathbf{3.0862}$$

(*c*) Conc. of OH^- in 200 mL of 0.1 M NaOH

$$= \frac{0.1\times200}{1000} = 0.02 \text{ mol}$$

Conc. of OH^- in 300 mL of 0.2 M KOH

$$= \frac{0.2\times300}{1000} = 0.06 \text{ mol}$$

Total moles of OH^- = 0.02 + 0.06 = 0.08 mol

Total volume = 200 + 300 = 500 mL

$$[OH^-] = \frac{0.08}{500}\times1000 = 0.16\ M$$

$$pOH = -\log(0.16) = 0.796$$

$$\therefore \quad pH = 14 - 0.796 = \mathbf{13.204}$$

❑ Example 66.

What will be the pH of a solution obtained by mixing 800 mL of 0.05 M NaOH and 200 mL of 0.1 M HCl assuming complete dissociation of the acid and the base?

Solution: No. of moles of NaOH in 800 mL of 0.05 M NaOH

$$= \frac{0.05}{1000}\times800 = 0.04 \text{ mol}$$

No. of moles of HCl in 200 mL of 0.1 M HCl

$$= \frac{0.1}{1000}\times200 = 0.02 \text{ mol}$$

0.02 mol of HCl will react with 0.02 mol of NaOH

Moles of NaOH left = 0.04 – 0.02 = 0.02 mol

Total volume of solution = 800 + 200 = 1000 mL

$$\text{Molar conc. of NaOH} = \frac{0.02}{1000}\times1000$$

$$= 0.02\ M$$

Since NaOH is completely dissociated

$$[OH^-] = [NaOH] = 0.02\ M = 2 \times 10^{-2}\ M$$

$$pOH = -\log(2 \times 10^{-2}) = 1.7$$

Now $pH + pOH = 14$

$$\therefore \quad pH = 14 - pOH = 14 - 1.7 = \mathbf{12.3.}$$

❑ Example 67.

Calculate the pH of a solution formed by mixing 0.2 M NH_4Cl and 0.1 M NH_3. The pK_b of ammonia is 4.75.

Solution : NH_3 is a weak base and ionises partially whereas, ammonium chloride ionises completely in the solution. Let x be the number of moles of ammonia ionised :

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

Since NH_4Cl is completely ionised, the concentration of NH_4^+ ions from NH_4Cl = 0.2 M

Total $[NH_4^+] = 0.2 + x \approx 0.2$

Total conc. of NH_3 left unionized = $0.1 - x \approx 0.1$ (because x is small)

So, at equilibrium

$$\underset{0.1}{NH_3} + H_2O \rightleftharpoons \underset{0.2}{NH_4^+} + \underset{x}{OH^-}$$

Now $pK_b = -\log K_b = 4.75$

$$\therefore \quad \log K_b = -4.75$$

$$K_b = \text{antilog}\ (-4.75) = 1.78 \times 10^{-5}$$

Now $$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.78 \times 10^{-5} = \frac{(0.20)x}{0.1}$$

$$\therefore \quad x = 0.89 \times 10^{-5}$$

$$\therefore \quad [OH^-] = 0.89 \times 10^{-5}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1\times10^{-14}}{0.89\times10^{-5}} = 1.12 \times 10^{-9}$$

$$pH = -\log[H_3O^+] = -\log(1.12 \times 10^{-9})$$

$$= \mathbf{8.95.}$$

Type F : Calculation of pH of very dilute acid or base solutions or solutions on dilution.

It may be noted that in an aqueous solution of strong acid, the main source of H^+ or H_3O^+ ions is the acid itself unless the solutions are very dilute. If the molarity of the solution is equal to or less than 10^{-6} M, then the H^+ and OH^- obtained by the ionization of the water has also to be considered as discussed in the following examples.

❑ Example 68.

Calculate the pH of 1×10^{-8} M solution of HCl

Solution: If we use the relation, $pH = -\log[H_3O^+]$, we get pH equal to 8. But this is not correct because an acidic solution cannot have *p*H greater than 7. It may be noted that in very dilute acidic solution, when H^+ concentrations from acid and water are comparable, the concentration of H^+ from water cannot be neglected. Therefore,

$$[H^+]_{total} = [H^+]_{acid} + [H^+]_{water}$$

Since HCl is a strong acid and is completely ionized

$$[H^+]_{HCl} = 1.0 \times 10^{-8}$$

The concentration of H^+ from ionization of water is equal to the $[OH^-]$ from water,

$$[H^+]_{H_2O} = [OH^-]_{H_2O} = x \text{ say}$$

$$[H^+]_{total} = 1.0 \times 10^{-8} + x$$

But $[H^+]\,[OH^-] = 1.0 \times 10^{-14}$

$$(1.0 \times 10^{-8} + x)\,(x) = 1.0 \times 10^{-14}$$

$$x^2 + 10^{-8}\,x - 10^{-14} = 0$$

Solving for x, we get $x = 9.5 \times 10^{-8}$

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$\therefore \quad [H^+] = 1.0 \times 10^{-8} + 9.5 \times 10^{-8} = 10.5 \times 10^{-8}$

$= 1.05 \times 10^{-7}$

$pH = -\log [H^+] = -\log (1.05 \times 10^{-7}) = \mathbf{6.98}$

Example 69.

Calculate the pH of 1×10^{-8} M NaOH solution.

Solution: If we use the relation, $pOH = -\log [OH^-]$, we get pOH equal to 8 and pH becomes 6 (14 – 8). But this is not correct because a basic solution cannot have pH less than 7. Therefore, for very dilute basic solutions, when OH^- concentrations from base and water are comparable, then concentration of OH^- from water cannot neglected. Therefore,

$$[OH^-]_{total} = [OH^-]_{base} + [OH^-]_{water}$$

The concentration of OH^- from dissociation of water is equal to the concentration of H^+ from water,

$$[OH^-]_{H_2O} = [H^+]_{H_2O} = x \text{ say}$$

$$[OH^-]_{total} = 1.0 \times 10^{-8} + x$$

But $[H^+][OH^-] = 1.0 \times 10^{-14}$

$x(1.0 \times 10^{-8} + x) = 1.0 \times 10^{-14}$

$1.0 \times 10^{-8}x + x^2 = 1.0 \times 10^{-14}$

$x^2 + 1.0 \times 10^{-8}x - 1.0 \times 10^{-14} = 0$

Solving for x, we get $x = 9.5 \times 10^{-8}$

$\therefore \quad [OH^-] = 1.0 \times 10^{-8} + 9.5 \times 10^{-8}$

$= 1.05 \times 10^{-7}$

$pOH = -\log (1.05 \times 10^{-7})$

$= 6.98$

$\therefore \quad pH = 14 - pOH$

$= 14 - 6.98 = \mathbf{7.02}.$

Example 70.

pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained by diluting the given solution 100 times?

Solution: $pH = 5$

or $-\log[H^+] = 5$

$\therefore \quad [H^+] = 10^{-5}$ M

On diluting 100 times, $[H^+] = \dfrac{10^{-5}}{100} = 10^{-7}$ M

From the formula, $pH = -\log[H^+]$, its pH comes out to be 7. It is not possible because an acidic solution cannot have pH = 7. Since the solution is dilute,

$$[H^+]_{total} = [H^+]_{acid} + [H^+]_{water}$$

Since HCl is strong acid,

$$[H^+]_{HCl} = 1.0 \times 10^{-7}$$

The concentration of H^+ from ionization of water is equal to the $[OH^-]$ from water

$$[H^+]_{H_2O} = [OH^-]_{H_2O} = x \text{ (say)}$$

But $[H^+][OH^-] = 1.0 \times 10^{-14}$

$(1 \times 10^{-7} + x)x = 1.0 \times 10^{-14}$

$1 \times 10^{-7}x + x^2 - 1.0 \times 10^{-14} = 0$

Solving, we get $x = 1.0 \times 10^{-7}$

$[H^+] = 1.0 \times 10^{-7} + 1.0 \times 10^{-7}$

$= 2.0 \times 10^{-7}$

$pH = -\log (2.0 \times 10^{-7})$

$= 7 - \log 2$

$= 7 - 0.3010 = \mathbf{6.6990}$

Practice Problems

71. Calculate the pH of a solution containing 2.0 g of NaOH per litre of the solution.

72. A solution was prepared by dissolving 0.63 g of nitric acid in 10 L of the solution. Calculate its pH.

73. Calculate the *p*H of solution prepared by dissolving 2 g of TlOH in 2 L of solution.

74. Calculate the pH of 0.002 M CH_3COOH if it is 2.3% ionised at this concentration.

75. Calculate the pH value of 0.15 M solution of acetic acid.

$$K_{CH_3COOH} = 1.8 \times 10^{-5}$$

76. Calculate the pH of the solution prepared by dissolving 0.3 g of NaOH in water to give 200 mL of solution.

77. The pH of a solution obtained by dissolving 0.025 mole of an acid (HA) in 250 ml of the aqueous solution was found to be 4.0. Calculate the dissociation constant of HA.

78. Calculate the pH of a solution obtained by diluting 25 ml of decinormal HCl to 500 ml assuming complete ionisation of HCl.

79. How many grams of NaOH must be dissolved in one litre of the solution to give it a pH value of 10.6 at 25°C.

80. The pH of 0.05 M aqueous solution of diethylamine is 12.0. Calculate its K_b.

81. The pH of 0.02 M solution of pyridinium hydrochloride is 3.44. Calculate the ionization constant of pyridine.

82. The ionization constant of acetic acid is 1.74×10^{-5}. Calculate the degree of dissociation of acetic acid in 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

83. Calculate the *p*H of a solution obtained by mixing 50 ml of 0.01 M $Ba(OH)_2$ solution with 50 ml of water.

84. The dissociation constant of aniline, $C_6H_5NH_2$ is 4.3×10^{-10} mol L^{-1}. Calculate the pH of a 0.01 M solution of aniline in water.

85. At what molar concentration, the *p*H of nitrous acid should be 2.0 ? ($K_a = 4.5 \times 10^{-4}$).

86. The *p*H of 0.005 M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pK_b.

87. If 0.561 KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH ?

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Answers to Practice Problems

71. 12.7
72. 3
73. 11.65
74. 4.34
75. 2.79
76. 12.57
77. 1×10^{-7}
78. 2.302
79. 1.59×10^{-2} g
80. 2.0×10^{-3}
81. 1.5×10^{-9}
82. 1.86%, 9.3×10^{-4} M, 3.03
83. 12
84. 8.32.
85. 0.222 M
86. 1.591×10^{-6}, 5.8
87. $[K^+] = [OH^-] = 0.05$,
$[H^+] = 2.0 \times 10^{-13}$ M, pH = 12.70

Hints & Solutions on page 94

RELATION BETWEEN K_a AND K_b

We have learnt that K_a and K_b give the strength of an acid and a base respectively. In case of a conjugate acid-base pair,they are related in a simple manner so that if one is known, the other can be calculated.

Conjugate acid and base are related as :

$$\text{Base} + H^+ \rightleftharpoons \text{Acid}$$

or $$\text{Acid} \rightleftharpoons H^+ + \text{Base}$$

Let us consider a weak acid, HA.

$$HA(aq) + H_2O \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a(HA) = \frac{[H_3O^+][A^-]}{[HA]} \quad \ldots (i)$$

The conjugate base, A^- behaves as a weak base in water,

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$K_b(A^-) = \frac{[HA][OH^-]}{[A^-]} \quad \ldots (ii)$$

Multiply eqn (i) and (ii), we get

$$K_a(HA) \times K_b(A^-) = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]}$$

$$= [H_3O^+][OH^-] = K_w$$

$$K_a(HA) \times K_b(A^-) = K_w$$

In general, for any acid

$$K_a(\text{acid}) \times K_b(\text{conjugate base}) = K_w$$

$$= 10^{-14} \text{ mol}^2 \text{ L}^{-2} \text{ at } 298 \text{ K}$$

Taking negative logarithms of both sides :

$$-\log K_a(\text{acid}) - \log K_b(\text{conjugate base}) = -\log K_w$$

$$pK_a + pK_b = pK_w$$

$$\text{At } 298 \text{ K}, pK_w = -\log 10^{-14} = 14$$

$$\therefore pK_a(\text{acid}) + pK_b(\text{conjugate base}) = 14 \text{ at } 298 \text{ K}.$$

SOLVED EXAMPLES

Example 71.

The ionization constant of aniline is 4.3×10^{-10} (i) Calculate the pH of 0.001M aniline solution. (ii) Calculate the degree of ionization of aniline in the solution.
(iii) Calculate ionization constant of the conjugate acid of aniline. **N.C.E.R.T.**

Solution : (i)

$$C_6H_5NH_2(aq) + H_2O \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$$

$$K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]}$$

If c is the initial concentration of $C_6H_5NH_3^+$ and x is degree of ionization, then at equilibrium:

$$C_6H_5NH_2(aq) + H_2O \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$$

$$c(1-x) \qquad cx \qquad cx$$

$$K_b = \frac{(cx)\times(cx)}{c(1-x)} = \frac{cx^2}{1-x}$$

Since x is very small, $1 - x \simeq 1$

$$\therefore \quad K_b = cx^2$$

$$\therefore \quad x = \sqrt{\frac{K_b}{c}} = \sqrt{\frac{4.3\times10^{-10}}{0.001}} = \mathbf{6.56 \times 10^{-4}}$$

Degree of ionization of aniline = 6.56×10^{-4}

(ii) $[OH^-] = c\alpha = 0.001 \times 6.56 \times 10^{-4} = 6.56 \times 10^{-7}$ M

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$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1\times10^{-14}}{6.56\times10^{-7}} = 1.52 \times 10^{-8}$$

$$pH = -\log [H_3O^+] = -\log (1.52 \times 10^{-8})$$
$$= -\log 1.52 + 8 = -0.182 + 8 = \mathbf{7.818}$$

(*iii*) To calculate the relation between a base and its conjugate acid, consider the equation :

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

Base Conjugate acid

$$K_a \times K_b = K_w$$

Now $K_b = 4.3 \times 10^{-10}$

$$\therefore K_a(\text{conjugate acid of aniline}) = \frac{K_w}{K_b}$$

$$= \frac{1 \times 10^{-14}}{4.3\times10^{-10}} = \mathbf{2.32 \times 10^{-5}}$$

❑ Example 72.

Calculate the degree of ionization and pH of a 0.05 M ammonia solution. The ionization constant of ammonia is 1.77 × 10^{-5}. Also calculate the ionization constant of the conjugate acid of ammonia. ***N.C.E.R.T.***

Solution : If c is the initial conc. of NH_3 and α is its degree of ionisation,

	NH_3	+ H_2O ⇌	NH_4^+	+ OH^-
Initial conc.	c		0	0
At equi.	c(1–α)		cα	cα

$$K_b = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} \approx c\alpha^2$$

$$\therefore \quad c\alpha^2 = 1.77 \times 10^{-5}.$$

$$\alpha = \left(\frac{1.77\times10^{-5}}{0.05}\right)^{1/2} = 1.88 \times 10^{-2}$$

Degree of ionization= 1.88×10^{-2}

$$[OH^-] = c\alpha = 0.05 \times 1.88 \times 10^{-2}$$
$$= 9.4 \times 10^{-4}\ M$$

$$[H_3O^+] = \frac{1\times10^{-14}}{9.4\times10^{-4}} = 1.06 \times 10^{-11}$$

$$[H_3O^+] = -\log (1.06 \times 10^{-11}) = \mathbf{10.973}$$

Now $K_a \times K_b = K_w$ for acid-base pair

$$K_a \text{ (conjugate acid of } NH_3) = \frac{K_w}{K_b}$$

$$= \frac{1\times10^{-14}}{1.77\times10^{-5}} = \mathbf{5.64 \times 10^{-10}}$$

❑ Example 73.

Calculate

(i) Dissociation constant of conjugate base of HF, $K_a = 6.8 \times 10^{-4}$

(ii) Dissociation constant of conjugate acid of CO_3^{2-}, $K_b = 2.1 \times 10^{-4}$

Solution: (*i*) We know that

$$HF \rightleftharpoons H^+ + F^-$$

K_a (acid) × K_b (conjugate base) = 1.0×10^{-14}

$$K_a = 6.8 \times 10^{-4}$$

$$K_b (F^-) = \frac{1.0\times10^{-14}}{6.8\times10^{-4}} = \mathbf{1.47 \times 10^{-11}}$$

(*ii*) $$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$

$$K_b (CO_3^{2-}) \times K_a (HCO_3^-) = 1 \times 10^{-14}$$

$$K_b (CO_3^{2-}) = 2.1 \times 10^{-4}$$

$$K_a (HCO_3^-) = \frac{1\times10^{-14}}{2.1\times10^{-4}} = \mathbf{4.76 \times 10^{-11}}$$

POLYPROTIC ACIDS AND BASES

Bronsted acids which can donate more than one proton are called **polyprotic acids** or **polybasic acids.** For example, oxalic acid and sulphuric acid have two ionizable protons per molecule of the acid, which can be donated. These are called *dibasic acids*. Phosphoric acid (H_3PO_4) which can donate three protons is called *tribasic* or *triprotic acid*.

The ionization reactions, for example, for a dibasic acid may be represented as :

$$H_2X(aq) \rightleftharpoons H^+(aq) + HX^-(aq)$$
$$HX^-(aq) \rightleftharpoons H^+(aq) + X^{2-}(aq)$$

The corresponding ionization constants are :

$$K_{a_1} = \frac{[H^+][HX^-]}{[H_2X]} \text{ and}$$

$$K_{a_2} = \frac{[H^+][X^{2-}]}{[HX^-]}$$

K_{a_1} and K_{a_2} are called the first and second ionization constants respectively of the acid H_2X. Similarly, for a tribasic acid like H_3PO_4. We have three ionization constants.

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$$

$$K_{a_1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$$

$$K_{a_2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$$

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$$K_{a_3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

The ionization constants of some common polybasic acids are given in Table 8.

For example, carbonic acid, H_2CO_3 has the following equilibria :

$$H_2CO_3\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_3^-\,(aq)$$

$$K_{a_1} = 4.3 \times 10^{-7}$$

$$HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CO_3^{2-}\,(aq)$$

$$K_{a_2} = 5.6 \times 10^{-11}$$

The conjugate base of H_2CO_3 in the first equilibrium, HCO_3^- acts as an acid for the second equilibrium forming in turn its own conjugate base, CO_3^{2-}. The equation for the overall reaction is :

$$H_2CO_3\,(aq) + 2H_2O\,(l) \rightleftharpoons 2H_3O^+\,(aq) + CO_3^{2-}$$

This equation is the sum of the two individual equations. It can be seen that the overall equilibrium constant is the product of the equilibrium constants for each contributing reaction :

$$K_a = \frac{[H_3O^+]^2[CO_3^{2-}]}{[H_2CO_3]}$$

$$= \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} \times \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]}$$

$$= K_{a_1} \times K_{a_2}$$

It can also be observed from Table 8 that higher order ionization constants are smaller than the lower order ionization constants *i.e.*,

$$K_{a_1} > K_{a_2} > K_{a_3} \ldots$$

Thus, ***the acidic strength of polyprotic acid decreases as protons are lost.***

Similarly, a polyacidic base is a species which can accept more than one proton. For example, CO_3^{2-} anion; oxalate anion $C_2O_4^{2-}$, are diacidic because they can accept two protons and phosphate anion, PO_4^{3-} is triacidic because it can accept three protons. They have the corresponding ionization constants as

$$K_{b_1}, K_{b_2}, K_{b_3} \ldots\ldots \text{ etc.}$$

COMMON ION EFFECT IN THE IONIZATION OF ACIDS AND BASES

The ionization of an acid gives hydrogen or hydronium ion and corresponding anion. If any one of the product is added to the acid solution, then the ionization of the acid moves towards the backward direction according to the Le-Chatelier's principle. As a result, the ionization of the acid suppresses and the acid is ionized to a lesser extent. For example, acetic acid (CH_3COOH) dissociates as :

$$CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H^+\,(aq)$$

and $$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

If hydrogen ions are added to the solution from any other source, it will combine with acetate ions in the solution and form unionized acetic acid. As a result, the degree of ionization of acetic acid will be reduced. Similar will be the effect when an anion is added to the equilibrium mixture from external sources. This is known as *common ion effect*. It is also discussed later in this chapter.

Let us illustrate this by considering the effect on pH of the solution by adding 0.05 M acetate ion to 0.05 M acetic acid solution.

Table 8. Ionization constants of some common polybasic acids at 298 K

Acid	K_{a_1}	K_{a_2}	K_{a_3}
Oxalic acid, $(COOH)_2$	5.9×10^{-2}	6.5×10^{-5}	
Ascorbic acid (Vitamin C)	7.4×10^{-4}	1.6×10^{-12}	
Sulphurous, acid, H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulphuric acid, H_2SO_4	very large	1.2×10^{-2}	
Phosphorous acid, H_3PO_3	1.0×10^{-2}	2.6×10^{-7}	
Carbonic acid, H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Hydrosulphuric acid, H_2S	1.3×10^{-7}	7.1×10^{-15}	
Tartaric acid, $C_2H_4O_2(COOH)_2$	6.0×10^{-4}	1.5×10^{-5}	4.0×10^{-7}
Citric acid, $C_3H_5O(COOH)_3$	7.4×10^{-4}	1.7×10^{-5}	
Phosphoric acid, H_3PO_4	7.6×10^{-3}	6.2×10^{-8}	2.2×10^{-13}

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Acetic acid ionizes as :

$$CH_3COOH\,(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Initial conc.	0.05	0	0.05
Conc. at eq.	0.05–x	x	0.05 + x

Let x be the extent of ionization of acetic acid, then

$$K_c = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(0.05+x)\times x}{(0.05-x)}$$

Since K_c is very small for weak acid, $K_c << 0.05$ and

$0.05 + x \approx 0.05$ and $0.05 - x = 0.05$

Thus,

$$K_c = \frac{0.05\times x}{0.05} = x$$

But K_c for $CH_3COOH = 1.8 \times 10^{-5}$

$\therefore \quad x = 1.8 \times 10^{-5}$

or $\quad x = [H^+] = 1.8 \times 10^{-5}M$

$$pH = -\log [H^+] = -\log (1.8 \times 10^{-5}) = \mathbf{4.74}$$

FACTORS AFFECTING ACID STRENGTH

We have learnt methods to compare quantitatively the strength of acids and bases in terms of K_a and K_b. But we may be interested to know as to why should some acids be stronger than others ? What factors are responsible for making them stronger or weaker. This is not a simple phenomenon and will be learnt in different chapters. In a simple way, we can interpret that the strength of an acid depends mainly on the strength and polarity of H–A bond.

In general, when strength of H–A bond decreases then the energy required to break the bond decreases. Consequently, H^+ is easily released as H^+ and HA becomes stronger acid. Similarly, when HA becomes more polar *i.e.*, the electronegativity difference between atoms (H and A) increases, there is significant charge separation and cleavage of bond becomes easier thereby increasing the acid strength. A simple comparison can be made in a period and a group.

(*a*) Hydro acids of the elements of a period

Acid strength of the binary hydroacids increases on going from left to right across a period of the periodic table. The pK_a values of some hydroacids are given below :

CH_4	NH_3	H_2O	HF
58	35	14	3
	PH_3	H_2S	HCl
	27	7	–7
	AsH_3	H_2Se	HBr
	21	4	–9
		H_2Te	HI
		3	–11

For example, the acid strength of the hydroacids of the elements of second period increases as :

$$CH_4 < NH_3 < H_2O < HF$$

This trend can be easily explained on the basis of electronegativity. As we move from carbon to fluorine, the electronegativity of these elements increases in the order :

$$C < N < O < F$$

With the increase in electronegativity, the element has more and more tendency to withdraw strongly the electron pair from H and, therefore, the ionic character generally increases. Consequently, *the release of hydrogen ion becomes more easy and acidic character increases.*

Similarly, the acidic character of hydroacids of third period increases in the same order as :

$$PH_3 < H_2S < HCl$$

(*b*) Hydro acids of the elements of a group

The relative strength of the hydroacids of a group increases as we go down the group. For example, the relative strength of the hydroacids of group 17 increases as :

$$HF < HCl < HBr < HI$$

Similarly in group 16,the acidic strength increases as :

$$H_2O < H_2S < H_2Se < H_2Te$$

This order is the reverse of that expected on the basis of electronegativity. For example, in group 17, fluorine is the most electronegative halogen, the electronegativity gradually decreases as we move towards iodine through chlorine and bromine as :

$$F > Cl > Br > I$$

Thus , the hydride HF should be more ionic in character than any other hydride, therefore, it should release H^+ most readily. Consequently, it should be strongest acid. Actually, it is just the reverse. This can be explained as :

The acidic strength depends upon two factors : electronegativity and the size of the central atom. As discussed above, the electronegativity factor does not explain the correct order. As we go down the group, the atomic size of the central atom increases. As a result, H–A bond strength decreases and so the acid strength increases. The effect of increase in size is more than the effect of electronegativity change. As we know the electronegativity difference between fluorine and iodine is only 1.5, however, the size of halogen becomes nearly double.

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Atom	F	Cl	Br	I
Electronegativity	4.0	3.0	2.8	2.5
Atomic size (Å)	0.64	0.99	1.14	1.33

Note. The strength of hydroacids of halogens can easily be explained on the basis of relative *basic strength of their conjugate bases.* An acid loses H^+ ion and forms a conjugate base as :

$$HX \rightleftharpoons H^+ + X^-$$

The conjugate base of HF, HCl, HBr and HI are F^-, Cl^-, Br^- and I^- respectively. As we move from F^- to I^-, the size of the ion increases and, therefore, its electron density decreases from F^- to I^-.

Ion	F^-	Cl^-	Br^-	I^-
Ionic size (Å)	1.36	1.81	1.95	2.16

With the decrease in electron density, its tendency to attract a proton also decreases. In other words, the basic character decreases as $F^- > Cl^- > Br^- > I^-$. Now, we know a weak conjugate base has strong acid and a strong conjugate base has a weak acid. Therefore, F^- being the strongest base, its conjugate acid HF is weakest acid. Similarly, I^- is the weakest base, its conjugate acid HI is strongest acid.

Thus, the acidity decreases as :

$$HI > HBr > HCI > HF$$

SOLVED EXAMPLES

❑ **Example 74.**

The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ion in its 0.1 M solution. How will this concentration be affected if the solution is 0.1 M HCl also ?

If the second dissociation constant of H_2S is 1.2×10^{-13}, calculate the concentration of S^{2-} ion under these conditions. **N.C.E.R.T.**

Solution:

	$H_2S \rightleftharpoons$	HS^- +	H^+
Initial conc.	0.1 M	0	0
After dissociation	0.10–x	x	x

where x is the amount of H_2S dissociated

$$K_{a_1} = \frac{[HS^-][H^+]}{[H_2S]} = 9.1 \times 10^{-8}$$

or $$\frac{x \times x}{(0.10 - x)} = 9.1 \times 10^{-8}$$

Assuming $x << 0.10$

$$\frac{x^2}{0.10} = 9.1 \times 10^{-8}$$

$$x^2 = 9.1 \times 10^{-8} \times 0.1 = 9.1 \times 10^{-9}$$

$$\therefore \quad x = (9.1 \times 10^{-2})^{1/2} = \mathbf{9.54 \times 10^{-5}}.$$

In the presence of 0.1 M HCl, suppose the amount of H_2S dissociated is y so that at equilibrium,

$[H_2S] = 0.1 - y \approx 0.1$, $[H^+] = 0.1\ y \approx 0.1$ M, $[HS^-] = y$M

$$K_a = \frac{0.1 \times y}{0.1} = 9.1 \times 10^{-8}$$

or $$y = \mathbf{9.1 \times 10^{-8}}.$$

To calculate concentration of S^{2-} ion, we are to consider the second dissociation constant :

$$H_2S \overset{K_{a_1}}{\rightleftharpoons} H^+ + HS^-$$

$$HS^- \overset{K_{a_2}}{\rightleftharpoons} H^+ + S^{2-}$$

Overall reaction

$$H_2S \rightleftharpoons 2H^+ + S^{2-}.$$

$$K_a = K_{a1} \times K_{a2} = 9.1 \times 10^{-8} \times 1.2 \times 10^{-13}$$
$$= 1.092 \times 10^{-20}$$

$$K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = 1.092 \times 10^{-20}.$$

Now, in 0.1 M solution of H_2S :

$[H^+] = 2x$, $[S^{2-}] = x$, $[H_2S] = 0.1 - x \approx 0.1$

$$\frac{(2x)^2 \times x}{0.1} = 1.092 \times 10^{-20}$$

$$4x^3 = 1.092 \times 10^{-21}$$

$$x^3 = 0.273 \times 10^{-21}$$

or $$x = (0.273 \times 10^{-21})^{1/3}$$
$$= \mathbf{6.49 \times 10^{-8}\ M}$$

In presence of 0.1 M HCl, suppose $[S^{2-}] = y$, then

$[H^+] = 0.1 + y \approx 0.1$ M, $[H_2S] = 0.1 - y \approx 0.1$ M

$$K_a = \frac{(0.1)^2 \times y}{0.1} = 1.09 \times 10^{-20}$$

or $$y = \mathbf{1.09 \times 10^{-19}\ M.}$$

❑ **Example 75.**

Calculate the degree of ionization of 0.05 M acetic acid if its pK_a is 4.74. How is the degree of dissociation affected when its solution is also (i) 0.01 M in HCl and (ii) 0.1 M in HCl

N.C.E.R.T.

Solution:

$$pK_a = 4.74$$
$$-\log K_a = 4.74$$
$$\log K_a = -4.74$$

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$\therefore$ K_a = Antilog ($\bar{5}$ + 0.26)
= 1.8×10^{-5}

If α is the degree of dissociation, then

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.8\times10^{-5}}{0.05}}$$

$= 1.90 \times 10^{-2} =$ **0.019**

(*i*) When the solution is also 0.01 M in HCl. In this case, the H^+ concentration arises from two sources *i.e.* from HCl and from ionization of acetic acid. Let the concentration of H^+ from acetic acid be x, then

$[H^+] = 0.01$ (from HCl) + x (from CH_3COOH)

$[CH_3COO^-] = x$, $[CH_3COOH] = 0.05 - x$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

$$= \frac{(0.01+x)\,x}{0.05-x} = 1.8 \times 10^{-5}$$

Since x is very small, $0.01 + x = 0.01$, $0.05 - x = 0.05$

$$\frac{0.01x}{0.05} = 1.8 \times 10^{-5}$$

or $$x = \frac{1.8\times10^{-5}\times0.05}{0.01} = 9.0 \times 10^{-5}\ \text{M}$$

Degree of ionization $= \frac{x}{c} = \frac{9.0\times10^{-5}}{0.05} = 1.8 \times 10^{-3}$

= **0.0018**

(*ii*) When the solution is 0.1 M in HCl

If y is the concentration of H^+ from CH_3COOH

$[H^+] = 0.1 + y \approx 0.1$ M, $[CH_3COO^-] = y$,

$[CH_3COOH] = 0.05 - y = 0.05$ M

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

$$= \frac{0.1\times y}{0.05} = 1.8 \times 10^{-5}$$

$$y = \frac{1.8\times10^{-5}\times0.05}{0.1} = 9.0 \times 10^{-6}$$

Degree of ionization $= \frac{y}{c} = \frac{9.0\times10^{-6}}{0.05} = 1.8 \times 10^{-4}$

= **0.00018**

❑ **Example 76.**

The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenate ion in 0.05 M solution of phenol? What will be the degree of ionization if the solution is also 0.01 M in sodium phenate?

Solution: Phenol, PhOH ionizes as :

$$PhOH + H_2O \rightleftharpoons PhO^- + H_3O^+$$

Since the value of ionization constant is small, the degree of ionization,

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.0\times10^{-10}}{0.05}}$$

= **4.47×10^{-5}**

$[PhO^-] = c\alpha = 0.05 \times 4.47 \times 10^{-5} =$ **2.23×10^{-6} M**

$[H_3O^+] = c\alpha = 0.05 \times 4.47 \times 10^{-5} = 2.23 \times 10^{-6}$ M

$pH = -\log [H_3O^+] = -\log (2.23 \times 10^{-6})$

$= -\log 2.23 + 6 = -0.0348 + 6 =$ **5.65**

When the solution is 0.01 M in sodium phenate (PhONa),

$$PhOH \rightleftharpoons PhO^- + H^+$$

$$PhONa \rightleftharpoons PhO^- + Na^+$$

Concentration of PhO^- from phenol = x (say)

Since sodium phenate is completely ionized, the concentration of phenate from sodium phenate = 0.01 M

Total $[PhO^-] = 0.01 + x$

Conc. of phenol left unionized = $0.05 - x$

Now x being very very small

$[PhO^-] = 0.01 + x = 0.01$

$[PhOH] = 0.05 - x = 0.05$

$$K_a = \frac{[PhO^-][H^+]}{[PhOH]}$$

$$1.0 \times 10^{-10} = \frac{0.01\times[H^+]}{0.05}$$

$$[H^+] = \frac{1.0\times10^{-10}\times0.05}{0.01} = 5.0 \times 10^{-10}$$

$[H^+] = 5.0 \times 10^{-10}$

$pH = -\log [H^+] = -\log (5 \times 10^{-10})$
$= -\log 5 + 10 = -0.70 + 10 =$ **9.30**

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❑ **Example 77.**

Calculate the pH of a 0.10 M ammonia solution. Calculate the pH after 50.0 mL of this solution is treated with 25.0 mL of 0.10 M HCl. The dissociation constant of ammonia, $K_b = 1.77 \times 10^{-5}$.

Solution: $NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.77\times10^{-5}$$

Before neutralization,

$[NH_4^+] = x$, $[OH^-] = x$, $[NH_3] = 0.10 - x \approx 0.10$

$$K_b = \frac{x\times x}{0.10} = 1.77 \times 10^{-5}$$

$$x^2 = 1.77 \times 10^{-6}$$

$$x = 1.33 \times 10^{-3}$$

$$[OH^-] = 1.33 \times 10^{-3}\ M$$

$$\therefore \quad [H^+] = \frac{1\times10^{-14}}{1.33\times10^{-3}} = 7.51 \times 10^{-12}$$

$$pH = -\log (7.51 \times 10^{-12}) = \mathbf{11.12}$$

Moles of HCl present in 25.0 mL of 0.1 M

$$= \frac{0.1}{1000}\times25 = 2.5 \times 10^{-3} \text{ mole}$$

Moles of NH_3 present in 50.0 mL of 0.1 M

$$= \frac{0.1}{1000}\times50 = \mathbf{5.0 \times 10^{-3}\ mol.}$$

On addition of 25.0 mL of 0.1 M HCl solution to 50 mL of 0.1 M NH_3(i.e. 5.0×10^{-3} mol), 2.5×10^{-3} mol of ammonia molecules are neutralized. The resulting 75 mL of solution contains 2.5×10^{-3} mole of NH_3 molecules and 2.5×10^{-3} mole of NH_4^+ ions.

Conc. of NH_3,

$$[NH_3] = \frac{2.5\times10^{-3}}{75}\times1000 = 0.033\ M$$

$$[NH_4^+] = 0.033\ M$$

The following equilibrium exists :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

If y is the degree of dissociation

$0.033-y$ $\quad$ y $\quad$ y

The final solution after neutralisation also contains 0.033 M of NH_4^+ ions.

Total concentration of NH_4^+, $[NH_4^+] = 0.033 + y$

Since y is very small,

$[NH_4OH] = 0.033$ M and $[NH_4^+] = 0.033$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$K_b = \frac{y\times0.033}{0.033} = 1.77\times10^{-5}\text{M}$$

$$\therefore \quad y = 1.77 \times 10^{-5} = [OH]^-$$

Now $$[H^+] = \frac{1\times10^{-14}}{[OH^-]}$$

$$= \frac{1\times10^{-14}}{1.77\times10^{-5}}$$

$$= 0.56 \times 10^{-9}$$

$$pH = -\log [H^+]$$

$$= -\log (0.56 \times 10^{-9}) = \mathbf{9.24}$$

Practice Problems

◑ **88.** Calculate the degree of ionization of dimethylammine in its 0.02 M solution. $K_b = 5.4 \times 10^{-4}$. What percentage of dimethylamine is ionized if the solution is also 0.01 M in NaOH ?

◑ **89.** The ionization constant of propanoic acid is 1.32×10^{-5}. Calculate the degree of ionization in its 0.05 M solution and its pH. What will be its degree of ionization if the solution is 0.01 M in HCl also ?

N.C.E.R.T.

◑ **90.** Phosphorous acid, H_3PO_3 is a diprotic acid with K_a values 5×10^{-2} mol L^{-1} and 2×10^{-5} mol L^{-1} respectively for its two stages. Calculate the pH of a 0.01 M solution of H_3PO_3 (*aq*).

◑ **91.** Calculate the pH of 0.02 M H_2S (aq) given that

$K_{a_1} = 1.3 \times 10^{-7}$, $K_{a_2} = 7.1 \times 10^{-15}$

◑ **92.** A saturated solution of H_2S in water has concetration of approximately 0.10 M. What is the pH of this soluton and equilibrium concentrations of H_2S, HS^- and S^{2-} ? Hydrogen sulphide is a diprotic acid and its dissociation constants are $K_{a_1} = 9.1 \times 10^{-8}$

$K_{a_2} = 1.3 \times 10^{-3}$ mol L^{-1} respectively

Answers to Practice Problems

◐ **88.** 0.164, 0.0054.

◐ **89.** $\alpha = 1.62 \times 10^{-2}$,

pH = 3.09, α (in the presence of HCl) $= 1.32 \times 10^{-3}$

◐ **90.** 1.651

◐ **91.** 4.29.

◐ **92.** pH = 4.02, $[H_3O^+] = 9.5 \times 10^{-5}$,

$[HS^-] = 9.5 \times 10^{-5}$ M and $[S^{2-}] = 1.3 \times 10^{-13}$ M.

Hints & Solutions on page 94

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Conceptual Questions 2

Q.1. What are the conjugate acid and conjugate base of water.

Ans. Conjugate acid = H_3O^+, Conjugate base = OH^-

Q. 2. What is the conjugate base of $[Al(H_2O)_6]^{3+}$ ion ?

Ans. $[Al(H_2O)_5OH]^{2+}$

Q. 3. What is the effect of temperature on the ionic product of water ? How will it change the pH value of a neutral solution ?

Ans. Ionic product of water is :

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

Ionic product $K_w = [H_3O^+]\,[OH^-]$

Ionic product increases with increase of temperature because the dissociation of water (endothermic reaction) increases with increase of temperature.

Now, $pH = -\log [H_3O^+]$.

with increase in concentration of H_3O^+ ions, the pH of the neutral solution will decrease.

Q. 4. What will be the pH of 1M Na_2SO_4 solution ?

Ans. Na_2SO_4 is salt of strong acid and strong base and its aqueous solution will be neutral. Therefore, its *p*H will be 7.

CONCEPTUAL QA

Q. 5. What happens to ionic product of water if some acid is added to it ?

Ans. Ionic product will remain unchanged.

Q. 6. What is pOH ? What is its value for neutral water at 25°C ?

Ans. pOH is defined as

$pOH = -\log [OH^-]$

At 25°C, its value is 7 for neutral water.

Q. 7. Why is ammonia termed as a base though it does not contain OH^- ions ?

Ans. The basic nature of ammonia is due to its tendency to donate electron pair. Therefore, it is a Lewis base.

Q. 8. Glycine is an α-amino acid. It exists in the form of Zwitter ion as $^+NH_3CH_2COO^-$. Write the formula of its (*i*) conjugate acid (*ii*) conjugate base.

Ans. Conjugate acid : $^+NH_3CH_2COOH$,

Conjugate base ; $NH_2CH_2COO^-$.

Q. 9. Ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature? ***N.C.E.R.T.***

Ans. For neutral water,

$$K_w = [H_3O^+]\,[OH^-] = 2.7 \times 10^{-14}$$
$$[H_3O^+] = [OH^-]$$
$$[H_3O^+]^2 = 2.7 \times 10^{-14}$$
$$[H_3O^+] = 1.643 \times 10^{-7}$$
$$pH = -\log (1.643 \times 10^{-7})$$
$$= -(0.2156 - 7) = \mathbf{6.75.}$$

Q. 10. What will be the decreasing order of basic strength of the following conjugate bases?

OH^-, RO^-, CH_3COO^-, Cl^-

Ans. Conjugate base of a weak acid is a strong base and conjugate base of a strong acid is a weak base.

$RO^- > OH^- > CH_3COO^- > Cl^-$

Q. 11. Arrange the following in the increasing order of pH:

KNO_3 (*aq*), CH_3COONa(*aq*), NH_4Cl(*aq*), $C_6H_5COONH_4$(*aq*)

Ans. $NH_4Cl\,(aq) < C_6H_5COONH_4\,(aq) < KNO_3(aq) < CH_3COONa$

Q. 12. On millilitre solution of 0.01 M HCl is added to 1 L of sodium chloride solution. What will be the pH of the resulting solution ?

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Ans. NaCl is neutral, it simply dilutes the HCl solution from 1 mL to 1000 mL so that

$$[H^+] = \frac{0.01}{1000} = 10^{-5}\ M$$

$$\therefore \quad pH = -\log(10^{-5}) = \mathbf{5}.$$

Q. 13. Calculate the pH of a 0.001 M solution of $Ba(OH)_2$ assuming it to be completely ionised.

Ans. $Ba(OH)_2$ ionises in water as :

$$Ba(OH)_2(aq) \rightleftharpoons Ba^{2+}(aq) + 2OH^-(aq)$$

Since $Ba(OH)_2$ is completely ionised, one mole of $Ba(OH)_2$ gives 2 moles of OH^- ions.

Therefore,

$$[OH^-] = 2[Ba(OH)_2] = 2 \times 0.001 = 0.002\ M$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{0.002} = 5 \times 10^{-12}$$

$$pH = -\log[H_3O^+] = -\log(5 \times 10^{-12})$$

$$= -(\log 5 + \log 10^{-12})$$

$$= -(0.699 - 12) = \mathbf{11.301}$$

CONCEPTUAL QA

Q. 14. 4.9 g of sulphuric acid is present in 500 mL of the solution. Calculate the pH of the solution.

Ans. Moles of sulphuric acid $= \frac{4.9}{98} = 0.05$

$$[H_2SO_4] = \frac{0.05}{500} \times 1000 = 0.1\ M$$

Sulphuric acid ionises as :

$$H_2SO_4 + 2H_2O \rightleftharpoons 2H_3O^+ + SO_4^{2-}$$

$$\therefore \quad [H_3O^+] = 2 \times [H_2SO_4] = 2 \times 0.1 = 0.2\ M$$

$$pH = -\log(0.2) = \mathbf{0.6990}$$

Q. 15. Which of the following has higher pH value in each of the following pairs.

(*i*) 0.1 M NaOH or 0.01 M NaOH

(*ii*) 0.1 M HCl or 0.01 M HCl

(*iii*) 0.1 M HCl or 0.1 M NaOH

(*iv*) 0.1 M CH_3COOH or 0.1 M HCl

(*v*) 0.01 M HCl or 0.01 M NaCl

Ans. (*i*) 0.1 M NaOH (*ii*) 0.01 M HCl (*iii*) 0.1 M NaOH (*iv*) 0.1 M CH_3COOH (*v*) 0.01 M NaCl

HYDROLYSIS OF SALTS

It is commonly observed that different salts, on dissolution in water do not always form neutral solutions. For example, aqueous solution of copper sulphate is acidic whereas the aqueous solution of sodium acetate is basic in character. However, salts of strong acids and strong bases such as sodium chloride form neutral solution. This is due to the fact that a salt on dissolution in water undergoes dissociation to form ions. These ions can interact with water molecules and thereby produce either an acidic or an alkaline solution. This process is called **hydrolysis.** Thus, **hydrolysis** is

the interaction of anion or cation of the salt with water to produce an acidic or basic solution.

Hydrolysis is reverse of neutralization.

The pH of the solution gets affected by this interaction. The cations of strong bases (such as Na^+, K^+, Rb^+, Ca^{2+}, Ba^{2+}, etc.) and anions of strong acids (such as Cl^-, Br^-, I^-, NO_3^-, etc.) do not hydrolyze and therefore, the solutions of salts formed by strong acids and strong bases are neutral and their pH is 7. On the other hand, the solutions of the salts formed by strong acids and weak bases are acidic *i.e.,* their pH is less than 7. While the solutions of strong bases and weak acids are basic and their *p*H is greater than 7. This can be easily explained by developing quantitative relationship between the *p*H of the salt solution, ionization constants of acids and bases and their concentrations.

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The equilibrium constant of hydrolysis reaction is called **hydrolysis constant.** Let us consider a salt MX, a salt of acid HX and base MOH. The general hydrolysis equilibria and hydrolysis constants are given here :

Hydrolysis of anion (A^-)

$$MX + H_2O \longrightarrow \underset{\text{Acid}}{HX} + \underset{\text{Base}}{MOH}$$
(Salt)

or $$X^- + H_2O \longrightarrow HX + OH^-$$

$$K_h = \frac{[HX][OH^-]}{[X^-]}$$

Hydrolysis of cation

$$M^+ + 2H_2O \longrightarrow MOH + H_3O^+$$

$$K_h = \frac{[MOH][H_3O^+]}{[M^+]}$$

The fraction of the total salt that gets hydrolysed at equilibrium is called **degree of hydrolysis.** It is written as h.

Relation of Hydrolysis constant and K_a and K_b

1. Hydrolysis of salts of weak acid and strong base

The hydrolysis of salts of weak acids and strong bases give alkaline solutions due to the presence of free OH^- ions. The examples of these types of salts are CH_3COONa, Na_2CO_3, Na_3PO_4, etc. For example, CH_3COONa is a salt of weak acid, CH_3COOH and strong base NaOH. It gets completely ionised in aqueous solution :

$$CH_3COONa(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$$

Acetate ion thus formed undergoes hydrolysis in water to give acetic acid and OH^- ions:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

Acetic acid being weak acid ($K_a = 1.8 \times 10^{-5}$) remains mainly unionised in solution. This results in increase of OH^- ions concentration in solution making it **alkaline**. The pH of such a solution is more than 7. Thus, the reaction of hydrolysis of CH_3COONa may also be written as:

$$CH_3COONa + H_2O \rightleftharpoons \underset{\text{Weak acid}}{CH_3COOH} + Na^+ + \mathbf{OH^-}$$

Let us consider, in general, the solutions of salts like MX formed by a strong base MOH and a weak acid HX. Since salt is a strong electrolyte, it is completely ionized into M^+ and X^- ions according to the equation,

$$MX(s) + H_2O(l) \longrightarrow M^+(aq) + X^-(aq)$$

Since M^+ is a cation of strong base, it remains as such in solution. But the anion X^- reacts with water to form unionized acid (HX). This process is known as hydrolysis and is represented by the equation :

$$X^-(aq) + H_2O(l) \rightleftharpoons HX(aq) + OH^-(aq)$$

This is also called **anion hydrolysis.**

Hydrolysis constant*

Assuming that the concentration of water remains constant, the equilibrium constant for the hydrolysis reaction called hydrolysis constant may be written as :

$$K_h = \frac{[HX][OH^-]}{[X^-]} \quad ...(i)$$

The following equilibria also exist in solution.

For weak acid HX,

$$HX \rightleftharpoons H^+ + X^-$$

So that $$K_a = \frac{[H^+][X^-]}{[HX]} \quad ...(ii)$$

Also $$K_w = [H^+][OH^-] \quad ...(iii)$$

Multiplying the numerator and denominator of the right hand of Eq. (i) by $[H^+]$, we get

$$K_h = \frac{[HX][OH^-]}{[X^-]} \times \frac{[H^+]}{[H^+]} = \frac{[HX][OH^-][H^+]}{[X^-][H^+]}$$

$$= \frac{K_w}{K_a}$$

$$\boxed{K_h = \frac{K_w}{K_a}} \quad ...(iv)$$

It is clear that *the hydrolysis constant, K_h of the salt is inversely proportional to the dissociation constant, K_a of the weak acid.* Therefore, *the weaker the acid, the greater is the hydrolysis constant of the salt.*

Degree of hydrolysis

Let the original concentration of the salt in the solution be c mol/litre and h is the degree of hydrolysis at that concentration.

	X^-	+ H_2O ⇌	HX	+	OH^-
Initial conc.	c		0		0
Conc. at equilibrium	$c(1-h)$		ch		ch

The hydrolysis constant,

$$K_h = \frac{[HX][OH^-]}{[X^-]}$$

$$= \frac{ch.ch}{c(1-h)} = \frac{ch^2}{(1-h)}$$

The quadratic equation can be solved by the usual method, but it is simplified if h is small. If h is very small as compared to 1, we can assume $1 - h \approx 1$.

$$K_h = ch^2$$

or $$h = \sqrt{\frac{K_h}{c}} \quad ...(v)$$

Substituting the value of K_h from Eq. (iv)

$$\boxed{h = \sqrt{\frac{K_w}{K_a.c}}} \quad ...(vi)$$

* The derivations are not in the syllabus of CBSE. These are given to strengthen the understanding.

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pH of the hydrolysed salt solution

$$[OH^-] = ch$$

$$\therefore \quad [H^+] = \frac{K_w}{[OH^-]} = \frac{K_w}{ch}$$

Substituting the value of h from Eq. (*vi*)

$$[H^+] = \frac{K_w}{c}\sqrt{\frac{K_a \cdot c}{K_w}}$$

or $$[H^+] = \sqrt{\frac{K_w \cdot K_a}{c}}$$

Now, $$pH = -\log [H^+]$$

$$= -\log\left(\frac{K_w . K_a}{c}\right)^{\frac{1}{2}}$$

$$\therefore \quad pH = -\frac{1}{2}[\log K_w + \log K_a - \log c]$$

Now, $$-\log K_w = pK_w - \log K_a = pK_a$$

$$\therefore \quad pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log c \qquad ...(vii)$$

or at 298 K ($pK_w = 14$), the equation becomes

$$pH = 7 + \frac{1}{2}[pK_a + \log c]$$

Thus, knowing the molar concentration c of the solution, K_a and K_w, the pH of the solution can be calculated.

2. Hydrolysis of salt of strong acid and weak base

The hydrolysis of salts of weak bases and strong acids give acidic solution due to the presence of free H^+ ions. The common examples are NH_4Cl, $CuSO_4$, $AlCl_3$, etc. For example, NH_4Cl is a salt of weak base, NH_4OH and strong acid HCl. It gets completely ionised in water as:

$$NH_4Cl\,(aq) \longrightarrow NH_4^+\,(aq) + OH^-\,(aq)$$

Ammonium, NH_4^+ ions undergo hydrolysis in water to form NH_4OH and H^+ ions.

$$NH_4^+(aq) + H_2O\,(l) \rightleftharpoons NH_4OH + H^+\,(aq)$$

Ammonium hydroxide is a weak base ($K_b = 1.8 \times 10^{-5}$) and therefore, remains almost unionised in solution. This results in increase in concentration of H^+ ions in solution making the solution **acidic.** The pH of NH_4Cl solution in water is less than 7. Thus, the hydrolysis of NH_4Cl in water may be written as:

$$NH_4Cl + H_2O \rightleftharpoons \underset{\text{Weak base}}{NH_4OH} + Cl^- + \mathbf{H^+}$$

In general, for a salt MX formed by a strong acid HX and a weak base MOH, when dissolved in water dissociates into cation, M^+ and anion X^-.

$$\underset{\text{Salt}}{MX\,(s)} + H_2O\,(l) \rightleftharpoons M^+\,(aq) + X^-\,(aq)$$

Since X^- is anion of strong acid, it remains as such in solution. But the cation M^+ reacts with water to form unionized base MOH. This process may be written as

$$M^+\,(aq) + H_2O\,(l) \rightleftharpoons MOH\,(aq) + H^+ \qquad ...(viii)$$

So, it is also called **cationic hydrolysis.**

Hydrolysis constant

The hydrolysis constant may be written as :

$$K_h = \frac{[MOH][H^+]}{[M^+]} \qquad ...(ix)$$

The following equilibrium also exist in solution. For weak base MOH,

$$MOH \rightleftharpoons M^+ + OH^-$$

$$K_b = \frac{[M^+][OH^-]}{[MOH]} \qquad ...(x)$$

and $$K_w = [H^+]\,[OH^-] \qquad ...(xi)$$

Multiplying the numerator and denominator of right hand side of Eq. (ix) by $[OH^-]$, we get

$$K_h = \frac{[MOH][H^+]}{[M^+]} \times \frac{[OH^-]}{[OH^-]}$$

$$= \frac{[MOH][H^+][OH^-]}{[M^+][OH^-]} = \frac{K_w}{K_b}$$

or $$K_h = \frac{K_w}{K_b} \qquad ...(xii)$$

Thus, *the hydrolysis constant is inversely proportional to dissociation constant of the base.* Therefore, the *weaker the base, the greater is the hydrolysis constant of the salt.*

Degree of hydrolysis

Let the original concentration of the salt in the solution be c mol/litre and h is the degree of hydrolysis at that concentration.

	M^+	+ H_2O $\rightleftharpoons$	MOH	+	H^+
Initial conc.	c		0		0
Conc. at equilibrium	$(1-h)$		ch		ch

Hydrolysis constant, $$K_h = \frac{[MOH][H^+]}{[M^+]}$$

$$= \frac{ch.ch}{c(1-h)} = \frac{ch^2}{1-h}$$

If h is very small in comparison to 1, we may assume, $1 - h \approx 1$, so that

$$K_h = ch^2$$

or $$h = \sqrt{\frac{K_h}{c}} \qquad ...(xiii)$$

Substituting the value of K_h from eq. (*xii*)

$$h = \sqrt{\frac{K_w}{K_b . c}} \qquad ...(xiv)$$

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pH of the hydrolysed salt solution

Now, $[H^+] = ch$

Substituting the value of h from eq. (*xiv*)

$$[H^+] = c\sqrt{\frac{K_w}{K_b . c}}$$

$$= \sqrt{\frac{K_w . c}{K_b}}$$

Now, $pH = -\log[H^+]$

$$= -\log\left(\frac{K_w . c}{K_b}\right)^{\frac{1}{2}}$$

$$pH = -\frac{1}{2}\log K_w - \frac{1}{2}\log c + \frac{1}{2}\log K_b$$

Now, $-\log K_w = pK_w$ and $-\log K_b = pK_b$

$$\mathbf{pH = \frac{1}{2}\,pK_w - \frac{1}{2}\,pK_b - \frac{1}{2}\log c} \quad \ldots (xv)$$

At 298 K ($pK_w = 14$), the equation becomes

$$pH = 7 - \frac{1}{2}(\log c + p K_b)$$

3. Salt of weak acid and a weak base

In this case, both the cation and anion undergo hydrolysis to the same or different extents. The resulting solution may be **neutral, acidic or basic** depending upon the relative strengths of acids and bases. Some common examples of such salts are CH_3COONH_4, $(NH_4)_2CO_3$, $AlPO_4$, etc. For example, consider the hydrolysis of CH_3COONH_4 which is a salt of weak acid and weak base. It gets ionised as:

$$CH_3COONH_4\,(aq) \longrightarrow CH_3COO^-\,(aq) + NH_4^+\,(aq)$$

Both the ions undergo hydrolysis in water as:

$$CH_3COO^-(aq) + NH_4^+\,(aq) + H_2O \rightleftharpoons \underset{\text{Weak acid}}{CH_3COOH} + \underset{\text{Weak base}}{NH_4OH}$$

Both CH_3COOH and NH_4OH being weak acid and weak base respectively remain partially unionised.

$$CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H^+\,(aq)$$

$$NH_4OH\,(aq) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

Since CH_3COOH ($K_a = 1.8 \times 10^{-5}$) and NH_4OH ($K_b = 1.8 \times 10^{-5}$) are of almost equal strength, the resulting solution will be neutral (pH = 7). The hydrolysis may be written as :

$$CH_3COONH_4 + H_2O \rightleftharpoons \underset{\text{Weak acid}}{CH_3COOH} + \underset{\text{Weak base}}{NH_4OH}$$

Let us consider a salt MX formed by weak acid HX and weak base MOH. The salt in aqueous solution is completely dissociated into ions as :

$$MX\,(s) + H_2O\,(l) \longrightarrow M^+\,(aq) + X^-\,(aq)$$

Since both the cation and anion are of weak base and weak acid respectively, both of these hydrolyse in water as

$$M^+\,(aq) + X^-\,(aq) + H_2O\,(l) \rightleftharpoons MOH\,(aq) + HX\,(aq)$$

Therefore, it involves **anion hydrolysis** as well as **cation hydrolysis**.

Hydrolysis Constant

The hydrolysis constant, K_h may be written as

$$K_h = \frac{[MOH][HX]}{[M^+][X^-]} \quad \ldots (xvi)$$

The following equilibria also exist in the solution for weak acid,

$$HX \rightleftharpoons H^+ + X^-$$

$$K_a = \frac{[H^+][X^-]}{[HX]} \quad \ldots (xvii)$$

For weak base

$$MOH \rightleftharpoons M^+ + OH^-$$

$$K_b = \frac{[M^+][OH^-]}{[MOH]} \quad \ldots (xviii)$$

and $K_w = [H^+][OH^-]$ ...(*xix*)

Multiplying and dividing Eq. (*xvi*) by $[H^+][OH^-]$

$$K_h = \frac{[MOH]\,[HX]\,[H^+]\,[OH^-]}{[M^+]\,[X^-][H^+]\,[OH^-]}$$

or $$= \frac{[MOH]}{[M^+][OH^-]} . \frac{[HX]}{[X^-][H^+]} . [H^+][OH^-]$$

$$K_h = \frac{K_w}{K_a \times K_b}$$

Degree of hydrolysis

Let the original concentration of the salt in the solution be c mole/litre and h is the degree of hydrolysis.

	M^+	$+ X^-$	$+ H_2O$	$\rightleftharpoons$	MOH	+ HX
Initial conc.	c	c			0	0
Conc. at equilibrium	$c(1–h)$	$c(1–h)$			ch	ch

$$K_h = \frac{ch \times ch}{c(1-h) \times c(1-h)} = \frac{h^2}{(1-h)^2}$$

Since h is very small, it may be neglected in comparison to 1, so that $1 - h \approx 1$

$\therefore$ $K_h = h^2$

or $h = \sqrt{K_h}$

$$h = \sqrt{\frac{K_w}{K_a \times K_b}} \quad \ldots . (xxi)$$

It may be noted that in this case **the degree of hydrolysis is independent of the concentration of the solution.** Further, the weaker the acid and the base, the greater is the degree of hydrolysis of the salt.

pH of the hydrolysed salt solution.

According to Eq. (*xvii*), for the dissociation of a weak acid, HA,

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

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or $[H^+] = K_a \frac{[HA]}{[A^-]}$

$= \frac{K_a.ch}{c(1-h)} = \frac{K_a h}{(1-h)}$

or $[H^+] = K_a.h \quad (\because 1-h \approx 1)$

$= K_a \sqrt{K_h}$

$= K_a \sqrt{\frac{K_w}{K_a.K_b}}$

$= \sqrt{\frac{K_w.K_a}{K_b}}$ ...(xxii)

Now $pH = -\log [H^+]$

or $pH = -\log \left(\frac{K_w.K_a}{K_b}\right)^{\frac{1}{2}}$

$pH = -\frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log K_b$

Now $-\log K_w = pK_w$; $-\log K_a = pK_a$ and $-\log K_b = pK_b$

or $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$ ...(xxiii)

or at 298 K (when $pK_w = 14$)

$pH = 7 + \frac{1}{2}(pK_a - pK_b)$

It is clear from the above equation that pH of the solution will depend upon the pK values of the acid and the base. According to Eq. (*xxiii*)

- If $pK_a < pK_b$, pH of the solution will be less than $\frac{1}{2}pK_w$ and consequently solution will be **acidic.**
- If $pK_a > pK_b$, then pH of the solution will be more than $\frac{1}{2}pK_w$ and hence solution will be **alkaline.**
- If $pK_a = pK_b$, pH of the solution will be equal to $\frac{1}{2}pK_w$ and hence solution will be **neutral.**

4. Salt of strong acid and strong base

In this case, neither the cation nor the anion undergoes hydrolysis. Therefore, the resulting solution is neutral. For example, aqueous solution of KCl is neutral. When dissolved in water, its ions K^+ and Cl^- have no tendency to react with the H^+ and OH^- ions of water. This is because, the possible products of such reaction are KOH and HCl, which are themselves completely dissociated. As a result, there is no change in the concentration of H^+ and OH^- ions and hence the solution continues to remain neutral.

$$KCl\,(aq) \longrightarrow K^+ + Cl^-$$
$$H_2O \longrightarrow H^+ + OH^-$$
$$K^+(aq) + Cl^-(aq) + H_2O \longrightarrow K^+(aq) + OH^-(aq) + Cl^-(aq) + H^+(aq)$$

Hence, it can be concluded that **the salts of strong acids and strong bases do not undergo hydrolysis and the resulting solution is neutral.**

Let us **sum up** the important relations of hydrolysis of different salts.

Salt of	Example	K_h Hydrolysis constant	h Degree of hydrolysis	pH of solution
Weak acid and strong base	CH_3COONa	$\frac{K_w}{K_a}$	$\sqrt{\frac{K_w}{K_a.c}}$	$\frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log c$
Strong acid and weak base	NH_4Cl	$\frac{K_w}{K_b}$	$\sqrt{\frac{K_w}{K_b.c}}$	$\frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log c$
Weak acid and weak base	CH_3COONH_4	$\frac{K_w}{K_a.K_b}$	$\sqrt{\frac{K_w}{K_a.K_b}}$	$\frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$
Strong acid and strong base	NaCl	Does not undergo hydrolysis		

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SOLVED EXAMPLES

Example 78.

The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.

N.C.E.R.T.

Solution: For a salt of weak acid and weak base

$$pH = 7 + \frac{1}{2}(pK_a - pK_b)$$
$$= 7 + \frac{1}{2}(4.76 - 4.75)$$
$$= 7 + \frac{1}{2}(0.01)$$
$$= 7 + 0.005 = 7.005$$

Example 79.

Calculate

(a) the hydrolysis constant

(b) the degree of hydrolysis and

(c) the pH of 0.1 M sodium acetate solution.

The dissociation constant of CH_3COOH at room temperature is 1.8×10^{-5}.

Solution: For sodium acetate, the hydrolysis reaction is

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

(*a*) The hydrolysis constant,

$$K_h = \frac{K_w}{K_a}$$
$$K_w = 1.0 \times 10^{-14},\ K_a = 1.8 \times 10^{-5}$$
$$\therefore \quad K_h = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \mathbf{5.56 \times 10^{-10}}$$

(*b*) The degree of hydrolysis is

$$h = \sqrt{\frac{K_w}{K_a \cdot c}}$$
$$= \sqrt{\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 0.1}} = \mathbf{7.42 \times 10^{-5}}$$

(*c*)
$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log c$$
$$pK_w = -\log(1 \times 10^{-14}) = 14$$
$$pK_a = -\log(1.8 \times 10^{-5}) = 4.745$$
$$\log c = \log(0.1) = -1$$
$$\therefore \quad pH = \frac{1}{2}(14) + \frac{1}{2}(4.745) - \frac{1}{2} \times 1$$
$$= 7 + 2.372 - 0.5 = \mathbf{8.87}$$

Note : pH can also be calculated from the general equation

$$[OH^-] = ch = 0.1 \times 7.42 \times 10^{-5} = 7.42 \times 10^{-6}$$
$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{7.42 \times 10^{-6}} = 1.35 \times 10^{-9}$$
$$\therefore \quad pH = -\log[H^+] = -\log(1.39 \times 10^{-9})$$
$$= -(-9 + 0.1303) = \mathbf{8.87}$$

Example 80.

Calculate the pH of 0.01 M NH_4Cl solution at 25°C. K_b for $NH_4OH = 1.81 \times 10^{-5}$.

Solution: The hydrolysis reaction is

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

pH of this solution is

$$pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log c$$
$$pK_w = -\log(1 \times 10^{-14}) = 14$$
$$pK_b = -\log(1.81 \times 10^{-5}) = 4.74$$
$$\log c = \log 0.01 = \log(1 \times 10^{-2}) = -2$$
$$\therefore \quad pH = \frac{1}{2}(14) - \frac{1}{2}(4.74) - \frac{1}{2}(-2)$$
$$= \mathbf{5.63}$$

Example 81.

Calculate the pH of a 0.1 M aqueous ammonium cyanide solution. Given $pK_a = 9.02$ and $pK_b = 4.76$.

Solution: pH of the solution is given as :

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$
$$pK_w = 14,\ pK_a = 9.02,\ pK_b = 4.76$$
$$\therefore \quad pH = \frac{1}{2}(14) + \frac{1}{2}(9.02) - \frac{1}{2}(4.76)$$
$$= 7 + 4.51 - 2.38 = \mathbf{9.13}$$

Example 82.

The pH of a 0.1 M solution of NH_4Cl is 5.127. Calculate

(i) the degree of hydrolysis

(ii) the hydrolysis constant and

(iii) dissociation constant of the base.

Solution: pH of the solution = 5.127

$$pH = -\log[H^+]$$
$$\log[H^+] = -pH = -5.127$$
$$\therefore \quad [H^+] = \text{antilog}(-5.127)$$
$$= 7.46 \times 10^{-6}$$

The hydrolysis reaction is

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

If h is the degree of hydrolysis

$$[H^+] = ch = 7.46 \times 10^{-6}$$

(*a*) Degree of hydrolysis,

$$h = \frac{7.46 \times 10^{-6}}{c}$$
$$= \frac{7.46 \times 10^{-6}}{0.1} = \mathbf{7.46 \times 10^{-5}}$$

(*b*) Hydrolysis constant,

$$K_h = ch^2$$
$$= 0.1 \times (7.46 \times 10^{-5})^2$$
$$= \mathbf{5.56 \times 10^{-10}}$$

(*c*) Now, $K_h = \frac{K_w}{K_b}$

or $K_b = \frac{K_w}{K_h}$

$$= \frac{1.0 \times 10^{-14}}{5.56 \times 10^{-10}} = \mathbf{1.80 \times 10^{-5}}$$

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Example 83.

Calculate

(a) the hydrolysis constant

(b) the degree of hydrolysis, and

(c) the pH of a 0.1M NH_4CN solution at 25°C.

$K_a = 4.0 \times 10^{-10}$, $K_b = 1.8 \times 10^{-5}$

Solution: The hydrolysis reaction is

$$NH_4^+ + CN^- + H_2O \rightleftharpoons NH_4OH + HCN$$

Hydrolysis constant,

(a) $K_h = \dfrac{K_w}{K_a \times K_b}$

$K_a = 4.0 \times 10^{-10}$, $K_b = 1.8 \times 10^{-5}$

$= \dfrac{1.0 \times 10^{-14}}{(4.0 \times 10^{-10}) \times (1.8 \times 10^{-5})}$

$= \mathbf{1.39}$

(b) Degree of hydrolysis, h

$h = \sqrt{K_h}$

$= \sqrt{1.39} = \mathbf{1.18}$

(c) pH of the solution is

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

$pK_w = 14$

$pK_a = -\log (4 \times 10^{-10}) = 9.40$

$pK_b = -\log (1.8 \times 10^{-5}) = 4.74$

$\therefore \quad pH = \frac{1}{2}(14) + \frac{1}{2}(9.40) - \frac{1}{2}(4.74) = \mathbf{9.33}$

Example 84.

A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine. **N.C.E.R.T.**

Solution: pH of pyridinium hydrochloride = 3.44

Pyridinium hydrochloride is a salt of weak base and strong acid. pH of the soluton is given as :

$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log c$$

$$3.44 = \frac{1}{2} \times 14 - \frac{1}{2} pK_b - \frac{1}{2} \log 0.02$$

$$3.44 = 7 - \frac{1}{2} pK_b - \frac{1}{2} \times (-1.698)$$

$$\frac{1}{2} pK_b = 7 + 0.849 - 3.44$$

$$\frac{1}{2} pK_b = 4.409$$

$$pK_b = 8.818$$

$$-\log K_b = 8.818$$

$$\log K_b = -8.818 = \bar{9}.182$$

$$K_b = \mathbf{1.52 \times 10^{-9}}.$$

Example 85.

Calculte (i) the hydrolysis of ammonium acetate at 298 K

(ii) degree of hydrolysis and

(iii) pH in its (a) 0.01 M and (b) 0.04 M solution

pK_a (CH_3COOH) = 4.76 and pK_b (NH_4OH) = 4.75

Solution:

(i) $pK_a = 7.76$

$-\log K_a = 4.76$

or $\log K_a = -4.76 = 5.24$

$\therefore \quad K_a = \text{anti log } (5.24) = 1.74 \times 10^{-5}$

$pK_b = 4.75$

$-\log K_b = 4.75$ or $\log K_b = -4.75 = 5.25$

$\therefore \quad K_b = \text{antilog } (5.25) = 1.78 \times 10^{-5}$

Now $K_h = \dfrac{K_w}{K_a \times K_b} = \dfrac{10^{-14}}{(K_a \times K_b) \times (1.78 \times 10^{-5})}$

$= \mathbf{3.23 \times 10^{-5}}$

(ii) Since K_h is very small

$h = (K_h)^{\frac{1}{2}} = (3.23 \times 10^{-5})^{\frac{1}{2}}$

$\therefore \quad h = \mathbf{5.68 \times 10^{-3}}$

pH of solution of salt of weak acid and weak base if

(iii) $pH = 7 + \frac{1}{2}(pK_a - pK_b)$

$= 7 + \frac{1}{2}(4.76 - 4.75)$

$= 7.005.$

Since pH is independent of concentration, it is same for (a) and (b).

Example 86.

The ionization constant of chloroacetic acid is 1.35×10^{-3}. What will be pH of 0.1 M acid and its 0.1 M sodium salt solution.

Solution:

(i) pH of acid solution

$[H^+] = \sqrt{K_a \times c}$

$K_a = 1.35 \times 10^{-3}$, c = 0.1 M

$[H^+] = \sqrt{1.35 \times 10^{-3} \times 0.1}$

$= \sqrt{1.35 \times 10^{-4}} = 1.16 \times 10^{-2}$

$pH = -\log [H^+]$

$= -\log (1.16 \times 10^{-2})$

$= 2 - 0.064$

$= \mathbf{1.936.}$

(ii) pH of 0.1 M sodium salt solution.

Sodium salt of chloro acetic acid is salt of weak acid and strong base. Hence,

$$pH = \frac{1}{2} [pK_w + pK_a + \log c]$$

$K_a = 1.35 \times 10^{-3}$

$pK_a = -\log K_a$

$= -\log (1.35 \times 10^{-3})$

$= -(0.1303 - 3) = 2.8697$

$pK_w = -\log 10^{-14} = 14$

$c = 0.1$ M, $\log c = \log (0.1) = -1$

$$pH = \frac{1}{2} [14 + 2.8697 - 1]$$

$= \mathbf{7.935.}$

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Practice Problems

93. Calculate :
(*a*) the hydrolysis constant
(*b*) degree of hydrolysis, and
(*c*) the pH of 0.01 M NH_4Cl at 25°C.
K_b (NH_4OH) = 1.81×10^{-5}.

94. Calculate the degree of hydrolysis of a decimolar solution of ammonium acetate at 25°C. $K_a(CH_3COOH) = 1.75 \times 10^{-5}$, $K_b(NH_4OH) = 1.81 \times 10^{-5}$.

95. Calculate the percentage hydrolysis of sodium acetate in 0.1M solution at 25°C assuming the salt to be completely dissociated. $K_a = 1.8 \times 10^{-5}$.

96. Calculate the *p*H of 0.1M ammonium acetate at 25°C. $K_a = K_b = 1.8 \times 10^{-5}$

97. Calculate degree of hydrolysis and *p*H of 0.25 NaCN solution at 25°C. $K_a = 4.8 \times 10^{-10}$.

98. Calculate the hydrolysis constant of ammonium acetate at 298 K and also the degree of hydrolysis and *p*H of its
(*i*) 0.01 M and 0.04 M solutions.
pK_a (CH_3COOH) = 4.76, pK_b (NH_4OH) = 4.75

99. Calculate the degree of hydrolysis and the *p*H of 0.02 M ammonium cyanide solution at 298 K.
K_b (NH_4OH) = 1.77×10^{-5}, K_a (HCN) = 4.99×10^{-10}
N.C.E.R.T.

100. The ionization constant of nitrous acid (HNO_2) is 4.5×10^{-4}. Calculate the pH of 0.04 M sodium nitrite solution and also its degee of hydrolysis.
N.C.E.R.T.

Answers to Practice Problems

93. (*a*) 5.52×10^{-10}
(*b*) 2.35×10^{-4} (*c*) 5.63
94. 5.62×10^{-3}
95. 0.00745%
96. 7
97. 9.13×10^{-3}, 11.36
98. $K_h = 3.25 \times 10^{-5}$, $h = 5.7 \times 10^{-3}$, pH = 7.005
same values for all concentrations.
99. h = 1.06, pH = 4.725
100. pH = 7.285, $h = 2.35 \times 10^{-5}$

Hints & Solutions on page 94

BUFFER SOLUTION

We have studied that the hydrogen ion concentration of water changes quite significantly, if a few drops of a strong acid or a base is added to it. Quite often in industrial processes, chemical processes and in biological processes, it is necessary to have a solution whose pH value does not alter appreciably on addition of small amounts of strong acids or strong bases. Many body fluids such as blood or urine have definite pH values and changes in its pH values indicate malfunctioning of the body. The control of pH is also very essential and important in many chemical and biochemical processes. Many medical and cosmetic formulations need a definite pH for their formulation and use. Such solutions are called **buffer solutions.** Thus, a **buffer solution** is

the solution which resists changes in the hydrogen ion concentration on the addition of small amount of acid or base.

In other words, such solutions maintain a fairly constant pH value and are known to possess ***reserve acidity*** and ***reserve basicity*** in them. **Human blood is an excellent example of natural buffer solution.** Blood maintains its pH value around 7.35 inspite of a wide variety of foods we take. Buffer solutions are of two types :

(*a*) Acidic buffer.

Acidic buffer solution contains equimolar quantities of a weak acid and its salt with strong base. For example, acetic acid (CH_3COOH) and sodium acetate (CH_3COONa). A solution containing equimolar quantities of acetic acid and sodium acetate maintains its pH value around 4.74.

(*b*) Basic buffer.

Basic buffer solution contains equimolar quantities of a weak base and its salt with a strong acid. For example, ammonium hydroxide (NH_4OH) and ammonium chloride (NH_4Cl). A solution containing equimolar quantities of ammonium hydroxide and ammonium chloride maintains its pH value around 9.25.

Some examples of common buffer solutions along with their pH values are given in Table 9.

Table 9. Some common buffer solutions.

Buffer Pair	pH
Acetic acid/sodium acetate	4.74
Formic acid/sodium formate	3.7
Boric acid/sodium borate	7.0 – 9.0
Ammonium hydroxide/ammonium chloride	9.25

It may be noted that an aqueous solution of a salt of weak acid and weak base can also act as the buffer *e.g.*, CH_3COONH_4, $(NH_4)_2CO_3$, $(NH_4)_3PO_4$, etc.

Buffer action

The ability of the buffer solution to resist the changes in pH value on the addition of small amount of an acid or a base, is called **buffer action.**

In order to understand the buffer action, let us consider an acidic buffer such as a solution containing an equimolar amounts of acetic acid and sodium acetate. The solution contains a large number of sodium (Na^+), acetate (CH_3COO^-) ions and also a large number of undissociated acetic acid molecules.

$$CH_3COONa(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$$

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Suppose, a few drops of HCl are added to this buffer solution. This would provide hydrogen (H^+) ions. These additional H^+ ions would combine with the large reserve of CH_3COO^- ions to form undissociated acetic acid molecules.

$$CH_3COO^-(aq) + H^+(aq) \rightleftharpoons CH_3COOH$$

From buffer From HCl Weakly ionised

Since the additional H^+ ions are neutralised by CH_3COO^- ions in the solution, there will be no change in its *p*H value. The **reserve basicity of the solution is due to acetate ions.**

On the other hand, if a few drops of NaOH are added to the buffer solution, it would provide OH^- ions. These OH^- ions will combine with H^+ ions present in the buffer solution to form unionised water molecules. This would result in the greater ionisation of acetic acid in order to restore the concentration of hydrogen ions to its original value.

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$
$$H^+ + OH^- \rightleftharpoons H_2O$$

(From buffer) (From base)

Since the additional OH^- ions are neutralised by acetic acid molecules, the *p*H of solution does not change appreciably. **The reserve acidity of the solution is due to undissociated acetic acid molecules.**

Similarly, in case of a *basic buffer* solution containing equimolar quantities of ammonium hydroxide and ammonium chloride, there is a large concentration of ammonium ions, chloride ions and undissociated ammonium hydroxide.

$$NH_4Cl(aq) \xrightarrow{\text{Water}} NH_4^+(aq) + Cl^-(aq)$$

When a few drops of HCl (*aq*) are added, the additional H^+ ions are neutralised by OH^- ions present in the buffer :

$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
$$OH^- + H^+(aq) \rightleftharpoons H_2O$$

(From buffer) (From acid)

As some of OH^- ions from NH_4OH combine with H^+ ions from the acid, it would result into greater ionisation of NH_4OH to restore the concentration of OH^- ions. Thus, **reserve basicity of the solution is due to the presence of undissociated ammonium hydroxide.**

On the other hand, when a few drops of NaOH are added to the buffer solution, the additional OH^- ions are neutralised by ammonium ions.

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_4OH$$

(Weak base)

Therefore, **reserve acidity of solution is due to the presence of ammonium ions.**

Designing Buffer solution

The acidic or basic buffer solution of a known pH can be prepared from the knowledge of pK_a or pK_b value of the weak acid or weak base.

Henderson–Hasselbalch equation and Preparation of Acidic or Basic Buffer

We can derive a general equation for calculating the pH of any buffer solution. Consider, a mixture of weak acid (HX) and its conjugate base.

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

$$K_a = \frac{[H_3O^+][X^-]}{[HX]} \quad ...(i)$$

Rearranging the above equation, we have

$$[H_3O^+] = K_a \frac{[HX]}{[X^-]}$$

Taking logarithm on both sides, we get

$$\log [H_3O^+] = \log K_a + \log \frac{[HX]}{[X^-]}$$

$$\text{or } -\log [H_3O^+] = -\log K_a - \log \frac{[HX]}{[X^-]}$$

$$\text{or } pH = pK_a + \log \frac{[X^-]}{[HX]}$$

$$\text{or } pH = pK_a + \log \frac{[\text{Conjugate base}, X^-]}{[\text{Acid}]} \quad ...(ii)$$

The expression (*ii*) is known as **Henderson – Hasselbalch equation.** The quantity $\frac{[X^-]}{[HX]}$ is the ratio of concentration of conjugate base (anion) of the acid and the acid present in the mixture. Since the acid is a weak acid, it ionizes to a very little extent so that the concentration of [HX] is negligibly different from the concentration of acid taken to form buffer. Therefore, the concentration of [HX] is taken as the original concentration of acid. Also most of the conjugate base [X^-] comes from the ionization of the salt of the acid. Therefore, the concentration of conjugate base may be taken as the concentration of salt. Thus, Eq. (*ii*) may be written as :

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad ....(iii)$$

If we take molar concentrations of the acid and its salt (conjugate base) same,

i.e., [Salt] = [Acid]

$\therefore$ $pH = pK_a$ because log 1 = 0.

Thus, ***for the same molar concentration of acid and salt, the pH of the buffer solution will be equal to the pK_a of acid.*** Therefore, for preparing the buffer solution of the required pH, we select that acid whose pK_a is close to the required pH. For example, pK_a value of acetic acid is 4.76. Therefore, pH of the buffer solution formed by acetic acid and sodium acetate taken in equal molar concentration will be around 4.76.

Similarly, for a basic buffer of weak base B and its conjugate acid, BH^+,

$$pOH = pK_b + \log \frac{[\text{Conjugate acid}, BH^+]}{[\text{Base}, B]} \quad ...(iv)$$

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or $\quad pOH = pK_b + \log \dfrac{[Salt]}{[Base]}$

Now pH + pOH = 14

$$\therefore \quad pH = 14 - pK_b - \log \frac{[Salt]}{[Base]} \qquad ...(v)$$

If molar concentration of base and its conjugate acid (cation or salt) is same then pOH of the buffer solution will be same as pK_b of the base and pH will be equal to $14 - pK_b$. For example, pK_b of NH_4OH is 4.745, therefore, pH of basic buffer containing same molar concentrations of the base and its salt wil be 14 – 4.745 = 9.255. Thus, a buffer of pH close to 9.255 can be prepared by taking ammonia solution and ammonium chloride solution of equal molar concentration.

It may be noted that pH of the buffer solution is not affected by dilution because ratio under the logarithmic term remains unchanged.

SOLVED EXAMPLES

Example 87.

Calculate the pH of a buffer solution containing 0.2 mole of NH_4Cl and 0.1 mole of NH_4OH per litre. K_b for $NH_4OH = 1.85 \times 10^{-5}$.

Solution: According to Henderson's equation

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

$$pK_b = -\log K_b = -\log 1.85 \times 10^{-5} = 4.733$$

$$\therefore \quad pOH = 4.733 + \log \frac{(0.2)}{(0.1)}$$

$$= 4.733 + 0.301 = 5.034$$

$$pH = 14 - pOH = 14 - 5.034 = \mathbf{8.966.}$$

Example 88.

How much CH_3COONa should be added to 1 litre of 0.1 M CH_3COOH to make a buffer of pH = 4.0 ? $K_a = 1.8 \times 10^{-5}$.

Solution: According to Henderson's equation

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

$$pK_b = \log K_a = -\log 1.8 \times 10^{-5} = 4.745$$

$$\therefore \quad 4.0 = 4.745 + \log \frac{[Salt]}{[0.1]}$$

$$\log \frac{[Salt]}{[0.1]} = -0.745 \quad \frac{[Salt]}{[0.1]} = 0.180$$

$$\text{or} \quad [Salt] = 0.1 \times 0.180$$

$$= \mathbf{1.80 \times 10^{-2}\ mol/litre.}$$

Example 89.

The ionization constant of formic acid is 1.8×10^{-4}. Around what pH will its mixture with sodium formate give buffer solution of higher capacity ? Calculate the ratio of sodium formate and formic acid in a buffer of pH 4.25.

Solution: Buffer capacity is defined as the rate of change of pH with number of moles of acid or base added.

$$\text{Buffer capacity} = \frac{d\,pH}{dn_{\text{acid or base}}}$$

dpH is the change in pH and dn acid or base is the number of moles of acid or base added. It has been found that the buffer capacity is maximum near pK_a of the acid provided the total number of moles of salt and acid remain constant.

Therefore,

$$pK_a = -\log (1.8 \times 10^{-4})$$

$$= -\log 1.8 + 4 = -0.26 + 4 = \mathbf{3.74}$$

It is the pH of high capacity buffer.

For buffer solution;

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

$$4.25 = 3.74 + \log \frac{[Salt]}{[Acid]}$$

$$\log \frac{[Salt]}{[Acid]} = 4.25 - 3.74 \text{ or } = 0.51$$

$$\therefore \quad \frac{[Salt]}{[Acid]} = \text{Antilog } (0.51) = \mathbf{3.24}$$

Example 90.

How much of 0.3 M ammonium hydroxide should be mixed with 30 mL of 0.2 M solution of ammonium chloride to give buffer solutions of pH 8.65 and 10 ($pK_b = 4.75$) ?

Solution: For basic buffer solution ;

$$pH = 14 - pK_b + \log \frac{[Base]}{[Salt]}$$

$$pH = 14 - 4.75 + \log \frac{[Base]}{[Salt]}$$

$$\text{or} \quad \log \frac{[Base]}{[Salt]} = pH - 9.25$$

(*i*) For buffer of pH = 8.65

$$\log \frac{[Base]}{[Salt]} = 8.65 - 9.25$$

$$\text{or} \quad \frac{[Base]}{[Salt]} = \text{Antilog } (-0.60) = 0.25$$

$$\text{or} \quad \frac{[NH_4OH]}{[NH_4Cl]} = \frac{\dfrac{0.3 \times V}{1000}}{\dfrac{0.2 \times 30}{1000}} = 0.25$$

$$V = \frac{0.25 \times 0.2 \times 30 \times 1000}{0.3 \times 1000}$$

$$= 5.02 \text{ mL}$$

Similarly for solution of pH = 10

$$\log \frac{[Base]}{[Salt]} = 10 - 9.25$$

$$\frac{[Base]}{[Salt]} = \text{antilog } 0.75 = 5.62$$

$$\therefore \quad \frac{\dfrac{0.3 \times V}{1000}}{\dfrac{0.2 \times 30}{1000}} = 5.62$$

$$\therefore \quad V = \frac{5.62 \times 0.2 \times 30 \times 1000}{0.3 \times 1000}$$

$$= \mathbf{12.94\ mL}$$

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❑ **Example 91.**

How much volume of 0.1 M CH_3COOH should be added to 50 mL of 0.2 M CH_3COONa solution to prepare a buffer soluion of pH 4.91. pK_a of AcH is 4.76.

Solution: Accoding to Henderson's equation

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

$$pH = 4.91,\ pK_a = 4.76$$

$$4.91 = 4.76 + \log \frac{[Salt]}{[Acid]}$$

$$\log \frac{[NaAc]}{[AcH]} = 4.91 - 4.76 = 0.15$$

$$\frac{[NaAc]}{[AcH]} = \text{antilog } (0.15) = 1.41$$

If V is the volume of 0.1 M AcH required

$$\frac{[NaAc]}{[AcH]} = \frac{\frac{0.2\times 50}{1000}}{\frac{0.1\times V}{1000}} = 1.41$$

$$\frac{0.2\times 50}{0.14\times V} = 1.41$$

or $$V = \frac{0.2\times 50}{0.1\times 1.41} = \mathbf{70.92\ mL}$$

Volume of 0.1 M acetic acid required = **70.92 mL**

Practice Problems

◑ **101.** Blood has pH of 7.40. Calculate the ratio of hydrogen carbonate ion HCO_3^- to H_2CO_3 carbonic acid in blood to maintain its pH value. pK_a (H_2CO_3) = 6.37.

◑ **102.** Calculate the pH of a buffer solution that is 0.04 M CH_3COONa and 0.08 M CH_3COOH at 25°C. $pK_a = 4.74$

◑ **103.** Sodium hypochlorite, NaClO is the active ingredient in many bleaches. Calculate the ratio of the concentration of ClO^- and HClO in a bleach having a pH adjusted to 6.50 by using strong acid and strong base.

Answers to Practice Problems

◐ **101.** 10.7 to 1 ◐ **102.** 4.4

◐ **103.** $9.48 \times 10^{-2} : 1$

Hints & Solutions on page 94

SOLUBILITY PRODUCT

We have already learnt that the solubility of ionic solids in water differs to a great extent. Some of the ionic solids are so soluble that they are hygroscopic in nature and absorb even water from the atmosphere. On the other extreme there are substances which have so little solubility that these are regarded as insoluble. There are some ionic solids which have solubility in between these extreme cases.

The solubility depends on a number of factors. Among these two important factors are the *lattice enthalpy of the salt* and the *solvation enthalpy of ions* in the solution. Lattice enthalpy is the amount of energy required to break one mole of solid salt into its ions. Greater the lattice enthalpy, more will be the energy required to break the lattice of the salt. On the other hand, solvation enthalpy is the amount of energy released when one mole of a solid salt gets dissolved in a solvent. For a salt to dissolve in a solvent, the strong forces of attraction between its ions (*i.e.*, lattice enthalpy) must be overcome by the ion-solvent interactions (*i.e.*, solvation enthalpy).

Therefore, a salt will be soluble in a solvent only when solvation enthalpy is more than lattice enthalpy. If solvation enthalpy is less than lattice enthalpy, the salt will be insoluble. The amount of solvation enthalpy depends on the nature of the solvent. In case of a non polar (covalent) solvent, solvation enthalpy is small and therefore, it is not sufficient to overcome the lattice enthalpy of the salt. Consequently, the salt does not dissolve in non polar solvents. However, salts are soluble in polar solvents in which solvation enthalpy is large enough to overcome lattice enthalpy. Each salt has its characteristic solubility which depends on the temperature.

On the basis of solubility, we can classify the salts into three main categories :

Category I	Soluble	Solubility > 0.1 M
Category II	Slightly soluble	Solubility between 0.01 and 0.1 M
Category III	Sparingly soluble	Solubility < 0.01 M

Solubility Product Constant

Let us consider the equilibrium between the sparingly soluble salts and its saturated solutions.

There are many compounds such as lead chloride ($PbCl_2$), silver chloride (AgCl), barium sulphate ($BaSO_4$), etc., which are very slightly soluble in water. These substances are called *sparingly soluble salts*. When these sparingly soluble salts are dissolved in water, an equilibrium is established between the undissolved solid salt and ions of the dissolved salt. For example, for a sparingly soluble compound like AgCl, the following equilibrium occurs between the undissolved solid salt and the silver and chloride ions in the saturated solution :

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

Applying the law of chemical equilibrium, we get

$$K = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

or $$K \times [AgCl] = [Ag^+][Cl^-]$$

The concentration of the pure solid substance remains constant. Therefore, the concentration of solid

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AgCl in the solid state *i.e.,* [AgCl] is constant at a particular temperature, no matter how much solid is present in contact with the solution. It follows that

$$K \times \text{constant} = K_{sp} = [Ag^+]\,[Cl^-]$$

where K_{sp} is known as **solubility product constant** or **simply solubility product.** Since the solubility of a salt usually varies widely with temperature, the numerical value of K_{sp} for a salt changes with temperature.

Similarly, for barium sulphate, the dissolution may be represented as :

$$BaSO_4(s) \overset{\text{Water}}{\rightleftharpoons} Ba^{2+}(aq) + SO_4^{2-}(aq)$$

Applying law of chemical equilibrium

$$K = \frac{[Ba^{2+}][SO_4^{2-}]}{[BaSO_4]}$$

or $$K[BaSO_4] = [Ba^{2+}][SO_4^{2-}]$$

or $$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

In general, if the sparingly soluble salt, $A_x\,B_y$ is in equilibrium with saturated solution of its ions, then

$$\underset{\text{(solid)}}{A_x\,B_y} = xA^{y+} + yB^{x-}$$

where A^{y+} and B^{x-} denote the positive and negative ions respectively and x and y represent the number of these ions in the formula of the electrolyte.

The solubility product expression is :

$$K_{sp} = [A^{y+}]^x\,[B^{x-}]^y$$

Expressions of solubility products of some sparingly soluble salts

$PbCl_2 \rightleftharpoons$	$Pb^{2+} + 2Cl^-$	$K_{sp} = [Pb^{2+}]\,[Cl^-]^2$
$BaSO_4 \rightleftharpoons$	$Ba^{2+} + SO_4^{2-}$	$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$
$Mg(OH)_2 \rightleftharpoons$	$Mg^{2+} + 2OH^-$	$K_{sp} = [Mg^{2+}]\,[OH^-]^2$
$Ag_2CrO_4 \rightleftharpoons$	$2Ag^+ + CrO_4^{2-}$	$K_{sp} = [Ag^+]^2\,[CrO_4^{2-}]$
$Ca_3(PO_4)_2 \rightleftharpoons$	$3Ca^{2+} + 2PO_4^{3-}$	$K_{sp} = [Ca^{2+}]^3\,[PO_4^{3-}]^2$
$Zr_3(PO_4)_4 \rightleftharpoons$	$3Zr^{4+} + 4PO_4^{3-}$	$K_{sp} = [Zr^{4+}]^3\,[PO_4^{3-}]^4$

Thus, the **solubility product** of a salt at a given temperature is

equal to the product of the concentrations of its ions in the saturated solution, with each concentration term raised to the power equal to the number of ions produced on dissociation of one mole of the substance.

Solubility products of some sparingly soluble salts are recorded in Table 10.

Table 10. Solubility products (K_{sp}) of some salts at 298 K.

Name of salt	Formula	K_{sp}
Silver chloride	AgCl	1.8×10^{-10}
Silver bromide	AgBr	5.0×10^{-13}
Silver iodide	AgI	8.3×10^{-17}
Silver chromate	Ag_2CrO_4	1.1×10^{-12}
Silver carbonate	Ag_2CO_3	8.1×10^{-12}
Silver sulphate	Ag_2SO_4	1.4×10^{-5}
Calcium flouride	CaF_2	5.3×10^{-9}
Calcium hydroxide	$Ca(OH)_2$	5.5×10^{-6}
Calcium sulphate	$CaSO_4$	9.1×10^{-6}
Cadmium sulphide	CdS	8.0×10^{-27}
Chromium hydroxide	$Cr(OH)_3$	6.3×10^{-31}
Cuprous bromide	CuBr	5.3×10^{-9}
Cuprous chloride	CuCl	1.7×10^{-6}
Cupric carbonate	$CuCO_3$	1.4×10^{-10}
Cupric hydroxide	$Cu(OH)_2$	2.2×10^{-20}
Cuprous sulphide	Cu_2S	2.0×10^{-47}
Cupric iodate	$Cu(IO_3)_2$	1.4×10^{-7}
Cupric oxalate	$Cu(C_2O_4)$	2.9×10^{-8}
Cupric sulphide	CuS	6.3×10^{-36}
Ferrous suphide	FeS	6.3×10^{-18}
Ferrous hydroxide	$Fe(OH)_2$	8.0×10^{-16}
Ferric hydroxide	$Fe(OH)_3$	1.0×10^{-38}
Lead bromide	$PbBr_2$	4.0×10^{-5}
Lead chloride	$PbCl_2$	1.6×10^{-5}
Lead sulphate	$PbSO_4$	1.6×10^{-8}
Lead carbonate	$PbCO_3$	7.4×10^{-14}
Lead fluoride	PbF_2	7.7×10^{-8}
Lead hydroxide	$Pb(OH)_2$	1.2×10^{-15}
Lead sulphide	PbS	8.0×10^{-28}
Barium chromate	$BaCrO_4$	1.2×10^{-10}
Barium fluoride	BaF_2	1.0×10^{-6}
Barium sulphate	$BaSO_4$	1.1×10^{-10}
Calcium carbonate	$CaCO_3$	2.8×10^{-9}
Mercuric sulphide	HgS	4.0×10^{-53}
Magnesium carbonate	$MgCO_3$	3.5×10^{-8}
Magnesium fluoride	MgF_2	6.5×10^{-9}
Magnesium hydroxide	$Mg(OH)_2$	1.8×10^{-11}
Mercurous chloride	Hg_2Cl_2	1.3×10^{-18}
Mercurous iodide	Hg_2I_2	4.5×10^{-29}
Zinc hydroxide	$Zn(OH)_2$	1.0×10^{-15}
Zinc sulphide	ZnS	1.6×10^{-24}
Zinc carbonate	$ZnCO_3$	1.4×10^{-11}
Stannous sulphide	SnS	1.0×10^{-25}
Thallous bromide	TlBr	3.4×10^{-6}
Thallous iodide	TlI	6.5×10^{-8}
Aluminium hydroxide	$Al(OH)_3$	3.7×10^{-15}

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Calculation of Solubility Product

The solubility product of a sparingly soluble salt may be calculated from its solubility at a given temperature. Let us illustrate this with some examples.

SOLVED EXAMPLES

Example 92.

The solubility of silver chloride (AgCl) in water at 25°C is 1.06×10^{-5} mol L^{-1}. Calculate the solubility product of AgCl at this temperature.

Solution: The solubility equilibrium of AgCl is :

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

One mole of AgCl in solution gives 1 mole of Ag^+ ions and 1 mole of Cl^- ions. Since the solubility of AgCl is 1.06×10^{-5} mol L^{-1}, it will give 1.06×10^{-5} mol L^{-1} of Ag^+ ions and 1.06×10^{-5} mol L^{-1} of Cl^- ions. Therefore,

$$[Ag^+] = 1.06 \times 10^{-5} \text{ mol } L^{-1},$$
$$[Cl^-] = 1.06 \times 10^{-5} \text{ mol } L^{-1}$$

Now, $K_{sp} = [Ag^+][Cl^-]$
$= (1.06 \times 10^{-5}) \times (1.06 \times 10^{-5})$
$= \mathbf{1.12 \times 10^{-10}}$

Example 93.

The solubility of SrF_2 in water is 1.2×10^{-2} g L^{-1}. Calculate the solubility product of the salt at room temperature (molecular mass of SrF_2 = 125.6).

Solution: The solubility equilibrium is :

$$SrF_2(s) \rightleftharpoons Sr^{2+}(aq) + 2F^-(aq)$$

Solubility of $SrF_2 = 1.2 \times 10^{-2}$ g L^{-1}

Molar solubility of $SrF_2 = \dfrac{1.2 \times 10^{-2}}{125.6} = 9.55 \times 10^{-5}$ mol L^{-1}

According to above equation, one mole of SrF_2 produces one mole of Sr^{2+} ions and two moles of F^- ions. Therefore,

$$[Sr^{2+}] = 9.55 \times 10^{-5} \text{ mol } L^{-1}$$
$$[F^-] = 2 \times 9.55 \times 10^{-5} = 19.1 \times 10^{-5} \text{ mol } L^{-1}$$
$$K_{sp} = [Sr^{2+}][F^-]^2$$
$$= (9.55 \times 10^{-5}) \times (19.1 \times 10^{-5})^2$$
$$= \mathbf{3.48 \times 10^{-12}}$$

Practice Problems

104. A saturated solution of calcium fluoride (CaF_2) in water on analysis was found to contain at 298 K is 1.7×10^{-3} g per 100 cm^3. Calculate the solubility product.

105. The solubility of silver chromate Ag_2CrO_4 is 8.0×10^{-5} mol L^{-1}. Calculate the solubility product.

106. Complete the statment. If solubility of $Al_2(SO_4)_3$ is x, its solubility product will be... .

107. Calculate the solubility product of AgCl if the solubility of the salt in saturated solution at 298 K is 0.00198 g L^{-1}.

108. The solubility of magnesium hydroxide [$Mg(OH)_2$] at 300° C is 8.35×10^{-3} g L^{-1}. Find out its K_{sp}. [Mol. wt. of $Mg(OH)_2$ = 58]

109. Calculate the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298 K from their solubility product constants. Determine the molarities of the individual ions. K_{sp} (Ag_2CrO_4) = 1.1×10^{-12}, K_{sp} ($BaCrO_4$) = 1.2×10^{-10}, K_{sp} $Fe(OH)_3$ = 1.0×10^{-38} K_{sp} $PbCl_2$ = 1.6×10^{-5}, K_{sp} (Hg_2I_2) = 4.5×10^{-29}.

Answers to Practice Problems

104. 4.14×10^{-11} **105.** 2.048×10^{-12}

106. $108\ x^5$ **107.** 1.9×10^{-10}

108. 1.194×10^{-11}.

109. 6.5×10^{-5} M, 1.09×10^{-5} M, 1.38×10^{-10} M, 1.59×10^{-2} M, 8.18×10^{-8}M.

Hints & Solutions on page 94

Importance of Solubility Product

The concept of solubility product is very useful in explaining many phenomena. It is commonly used in predicting the solubility and precipitation of compounds in analytical chemistry.

1. Calculation of solubility. Knowing the solubility product of a sparingly soluble salt like AgCl, $BaSO_4$, Ag_2CrO_4, $Mg(OH)_2$, PbI_2, etc., the solubility of the salt can be calculated.

For example, consider a salt like zirconium phosphate, $Zr_3(PO_4)_4$. It dissociates as :

$$Zr_3(PO_4)_4 \rightleftharpoons 3Zr^{4+} + 4\ PO_4^{3-}$$

If s is the solubility of the salt, then from the stoichiometry of the compound,

$$[Zr^{4+}] = 3s \text{ and } [PO_4^{3-}] = 4s$$

So that

$$K_{sp} = [Zr^{4+}]^3\ [PO_4^{3-}]^4$$
$$= (3s)^3\ (4s)^4 = 6912\ s^7$$

or solubility $s = \left(\dfrac{K_{sp}}{6912}\right)^{1/7}$

In general, for a salt like $A_x B_y$ which ionises as :

$$A_x B_y \rightleftharpoons x\ A^{p+}(aq) + y\ B^{q-}(aq)$$

(where $xp^+ = yq^-$)

If s is solubility of the salt, then according to stoichiometry of the compound.

$$[A^{p+}] = x\ s \text{ and } [B^{q-}] = ys$$
$$K_{sp} = [A^{p+}]^x\ [B^{q-}]^y$$
$$= (xs)^x\ (ys)^y$$
$$= x^x y^y\ s^{x+y}$$

or $s^{x+y} = K_{sp}/x^x y^y$

or $s = \left(\dfrac{K_{sp}}{x^x y^y}\right)^{\frac{1}{x+y}}$

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SOLVED EXAMPLES

Example 94.

The solubility product of silver bromide is 3.3×10^{-13}. Calculate its solubility.

Solution: The solubility equilibrium is :

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

Thus, $K_{sp} = [Ag^+]\,[Br^-]$

Let the solubility of AgBr be s mol L^{-1}, then s moles of AgBr dissolved will give s moles of Ag^+ and s moles of Br^- ions. That is

$$[Ag^+] = s, [Br^-] = s$$

$$\therefore \quad K_{sp} = [Ag^+]\,[Br^-] = s \times s$$

$$\text{or} \quad 3.3 \times 10^{-13} = s^2$$

$$\text{or} \quad s = \sqrt{3.3 \times 10^{-13}} = \sqrt{33 \times 10^{-14}}$$

$$= \sqrt{33} \times 10^{-7} = \mathbf{5.74 \times 10^{-7}\ mol\ L^{-1}}$$

Example 95.

Calculate the solubility of $PbCl_2$ if its solubility product is 1.0×10^{-6} at 298 K.

Solution: The solubility equilibrium is :

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

Suppose the solubility of $PbCl_2$ is s moles per litre. Then the concentrations of various species at equilibrium are :

$$[Pb^{2+}] = s, [Cl^-] = 2s$$

Now, $K_{sp} = [Pb^{2+}]\,[Cl^-]^2$

$$1.0 \times 10^{-6} = (s) \times (2s)^2$$

$$1.0 \times 10^{-6} = 4s^3$$

$$\text{or} \quad s^3 = \frac{1.0 \times 10^{-6}}{4}$$

$$\text{or} \quad s = 6.3 \times 10^{-3}\ \text{mol}\ L^{-1}$$

Thus, solubility of $PbCl_2$ = $\mathbf{6.3 \times 10^{-3}\ mol\ L^{-1}}$

Example 96.

Calculate the solubility of A_2X_3 in pure water assuming that neither type of ion reacts with water. The solubility product of A_2X_3, $K_{sp} = 1.1 \times 10^{-23}$.

N.C.E.R.T.

Solution: The solubility equilibrium is :

$$A_2X_3 \rightleftharpoons 2A^{3+} + 3X^{2-}$$

Suppose the solubility of A_2X_3 is s mol L^{-1}, then concentration of various species at equilibrium are :

$$[A^{3+}] = 2s, [X^{2-}] = 3s$$

$$K_{sp} = [A^{3+}]^2\,[X^{2-}]^3$$

$$= (2s)^2 \times (3s)^3$$

$$= 108s^5$$

$$\therefore \quad 108\ s^5 = 1.1 \times 10^{-23}$$

$$s^5 = \frac{1.1 \times 10^{-23}}{108} = 1.01 \times 10^{-25}$$

$$\therefore \quad s = \mathbf{1 \times 10^{-5}\ mol\ L^{-1}}$$

Example 97.

The K_{sp} value of two sparingly soluble salts $Ni(OH)_2$ and AgCN are 2.0×10^{-15} and 6.0×10^{-17} respectively. Which salt is more soluble ?

Solution:

$$AgCN \rightleftharpoons Ag^+ + CN^-$$

Suppose the solubility of AgCN is x mol L^{-1} so that

$$[Ag^+] = x, \ [CN^-] = x$$

$$K_{sp} = [Ag^+]\,[CN^-]$$

$$= x \times x = x^2$$

$$\text{or} \quad x = (K_{sp})^{1/2} = (6.0 \times 10^{-17})^{1/2}$$

$$= \mathbf{7.75 \times 10^{-9}}$$

$$Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$$

Let solubility of $Ni(OH)_2$ is y mol L^{-1} so that

$$[Ni^{2+}] = y, [OH^-] = 2y$$

$$K_{sp} = [Ni^{2+}]\,[OH^-]^2$$

$$= y \times (2y)^2 = 4y^3$$

$$\therefore \quad y = \left(\frac{K_{sp}}{4}\right)^{1/3}$$

$$= \left(\frac{2.0 \times 10^{-15}}{4}\right)^{1/3}$$

$$= (0.5 \times 10^{-15})^{1/3}$$

$$\text{or} \quad \mathbf{y = 7.93 \times 10^{-5}}$$

$Ni(OH)_2$ is more soluble than AgCN.

Example 98.

The solubility product of lead bromide is 8×10^{-5} at 298 K. If the salt is 80% dissociated in saturated solution, calculate the solubility of the salt (in gram / litre).

Solution: The solubility equilibrium is :

$$PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-$$

Suppose the solubility of $PbBr_2$ is s moles per litre. Then the concentrations of various species at equilibrium are :

$$[Pb^{2+}] = s, [Br^-] = 2s$$

Now, $K_{sp} = [Pb^{2+}][Br^-]^2$

$$8 \times 10^{-5} = (s) \times (2s)^2$$

$$8 \times 10^{-5} = 4s^3$$

$$\text{or} \quad s^3 = \frac{8 \times 10^{-5}}{4} = 2 \times 10^{-5}$$

$$s = (2.0 \times 10^{-5})^{1/3} = 2.714 \times 10^{-2}\ \text{mol}\ L^{-1}$$

This is the solubility of $PbBr_2$ if it is 100% dissociated.

Solubility of $PbBr_2$ if it is 80% dissociated

$$= \frac{2.714 \times 10^{-2} \times 80}{100}$$

$$= 2.192 \times 10^{-2}\ \text{mol}\ L^{-1}$$

Mol. wt. of $PbBr_2 = 207 + 2 \times 80 = 367$

$\therefore$ Solubility of $PbBr_2 = 2.192 \times 10^{-2} \times 367 = \mathbf{8.04\ g\ L^{-1}}$

Example 99.

The solubility product of AgCl in water is 1.5×10^{-10}. Calculate its solubility in 0.01 M NaCl aqueous solution.

Solution: NaCl dissociates completely as :

$$NaCl \longrightarrow Na^+ + Cl^-$$

Concentration of Cl^- ion in 0.01 M NaCl solution is

$$[Cl^-] = 0.01\ M$$

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Let solubility of AgCl in 0.01 M NaCl be x mol L^{-1}, then

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$[Ag^+] = x$ mol L^{-1}, $Cl^-(aq) = x$ mol L^{-1}

Total $[Cl^-] = 0.01 + x \approx 0.01$ M ($\because x$ is very small)

Now, $K_{sp} = [Ag^+][Cl^-]$

$= x \times 0.01 = 0.01\,x$

$\therefore \quad 0.01\,x = 1.5 \times 10^{-10}$

or $x = \dfrac{1.5\times10^{-10}}{0.01} = \mathbf{1.5 \times 10^{-8}\ mol\ L^{-1}.}$

❑ Example 100.

Calculate the solubility of AgCl, $Fe(OH)_3$, Ag_2SO_4 and Hg_2Br_2 from their solubility products. K_{sp} (AgCl) = 1.8 × 10^{-10}, K_{sp} [$Fe(OH)_3$] = 1.0 × 10^{-38}, K_{sp} [Ag_2SO_4] = 1.4 × 10^{-5}, K_{sp} (Hg_2Br_2) = 5.6 × 10^{-23}. Also calculate the solubilities of salts in gL^{-1} and molarities of the ions. **N.C.E.R.T.**

Solution: (*i*) $AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$

$K_{sp} = 1.8 \times 10^{-10}$

Let solubility be s moles per litre. Then the concentration of various species at equilibrium are :

$[Ag^+] = s, [Cl^-] = s$

$K_{sp} = [Ag^+]\,[Cl^-] = s \times s$

$1.8 \times 10^{-10} = s^2$

$\therefore \quad s = (1.8 \times 10^{-10})^{1/2} = 1.34 \times 10^{-5}$ mol L^{-1}

Solubility in g L^{-1} $= 1.34 \times 10^{-5} \times 143.5$

$= \mathbf{1.92 \times 10^{-3}\ gL^{-1}}$

$[Ag^+] = s = 1.34 \times 10^{-5}$ mol L^{-1}

$[Cl^-] = s = 1.34 \times 10^{-5}$ mol L^{-1}

(*ii*) For $Fe(OH)_3$: $K_{sp} = 1.0 \times 10^{-38}$

$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$

If solubility is s, then

$[Fe^{3+}] = s, [OH^-] = 3s$

$K_{sp} = [Fe^{3+}]\,[OH^-]^3$

$1.0 \times 10^{-38} = s \times (3s)^3 = 27s^4$

$27\,s^4 = 1.0 \times 10^{-38}$

$s^4 = \dfrac{1.0\times10^{-38}}{27}$

or $s = \left(\dfrac{1.0\times10^{-38}}{27}\right)^{1/4}$

$= 1.39 \times 10^{-10}$ mol L^{-1}

Solubility in g L^{-1} $= 1.39 \times 10^{-10} \times 106.5$

$= 1.48 \times 10^{-8}$ g L^{-1}

$[Fe^{3+}] = s = 1.39 \times 10^{-10}$ mol L^{-1}

$[OH^-] = 3s = 3 \times 1.39 \times 10^{-10}$

$= 4.17 \times 10^{-10}$ mol L^{-1}

(*iii*) For Ag_2SO_4 : $K_{sp} = 1.4 \times 10^{-5}$

$Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO_4^{2-}$

If solubility is s, then

$[Ag^+] = 2s, [SO_4^{2-}] = s$

$K_{sp} = [Ag^+]^2\,[SO_4^{2-}]$

$1.4 \times 10^{-5} = (2s)^2\,(s)$

$1.4 \times 10^{-5} = 4s^3$

or $s^3 = \dfrac{1.4\times10^{-5}}{4}$

$s = \left(\dfrac{1.4\times10^{-5}}{4}\right)^{\frac{1}{3}}$

$= 1.52 \times 10^{-2}$ mol L^{-1}

Solubility in gL^{-1} $= 1.52 \times 10^{-2} \times 312$

$= 4.74$ g L^{-1}

$[Ag^+] = 2s = 2 \times 1.52 \times 10^{-2}$

$= 3.04 \times 10^{-2}$ mol L^{-1}

$[SO_4^{2-}] = s = 1.52 \times 10^{-2}$ mol L^{-1}

(*iv*) For Hg_2Br_2 ; $K_{sp} = 5.6 \times 10^{-23}$

$Hg_2Br_2 \rightleftharpoons Hg_2^{2+} + 2Br^-$

If solubility is s, then

$[Hg_2^{2+}] = s, Br^- = 2s$

$K_{sp} = (s)\,(2s)^2$

$5.6 \times 10^{-23} = 4s^3$

or $4s^3 = 5.6 \times 10^{-23}$

$s = \left(\dfrac{5.6\times10^{-23}}{4}\right)^{1/3}$

$= 2.41 \times 10^{-8}$ mol L^{-1}

Solubility in g L^{-1} $= 2.41 \times 10^{-8} \times 360.4$

$= 8.68 \times 10^{-6}$ gL^{-1}

$[Hg_2^{2+}] = 2.41 \times 10^{-8}$, $[Br^-]$

$= 2 \times 2.41 \times 10^{-8}$

$= 4.82 \times 10^{-8}$ M

❑ Example 101.

The solubility product of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

Solution: For Ag_2CrO_4 $K_{sp} = 1.1 \times 10^{-12}$

If s is the solubility

$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$[Ag^+] = 2s, CrO_4^{2-} = s$

$K_{sp} = (2s)^2\,(s) = 4s^3$

$4s^3 = K_{sp} \quad \therefore s = \left(\dfrac{K_{sp}}{4}\right)^{\frac{1}{3}}$

$s = \left(\dfrac{1.1\times10^{-12}}{4}\right)^{\frac{1}{3}} = 6.50 \times 10^{-5}$ mol L^{-1}

For AgBr, $K_{sp} = 5.0 \times 10^{-13}$

If s is the solubility,

$[Ag^+] = s, [Br^-] = s$

$K_{sp} = (s) \times (s) = s^2$

$s^2 = K_{sp}$

$s = (5.0 \times 10^{-13})^{1/2} = 7.07 \times 10^{-7}$ mol L^{-1}

Ratio of the molarities of the saturated solutions

$= \dfrac{6.50\times10^{-5}}{7.07\times10^{-7}} = \mathbf{91.9\ times.}$

❑ Example 102.

Calculate the solubility product of barium sulphate in 0.05 M barium chloride solution. K_{sp} of $BaSO_4$ = 1.1 × 10^{-10}. **N.C.E.R.T.**

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Solution: $BaCl_2$ dissociates ompletely as :

$$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$$

Conc. of Ba^{2+} in 0.05 M $BaCl_2$ solution is

$$[Ba^{2+}] = 0.05 \text{ M}$$

Let solubility of $BaSO_4$ is 0.05 M $BaCl_2$ solution be x mol L^{-1}.

Then

$$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$$

$$[Ba^{2+}] = x \text{ mol } L^{-1}, [SO_4^{2-}] = x \text{ mol } L^{-1}$$

$$\text{Total } [Ba^{2+}] = 0.05 + x \approx 0.05 \text{ M}$$

($\because$ x is very small)

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

$$= (0.05) \times x$$

or $$0.05\, x = 1.1 \times 10^{-10}$$

$$x = \frac{1.1 \times 10^{-10}}{0.05}$$

$$= \mathbf{2.2 \times 10^{-9} \text{ mol } L^{-1}}.$$

❑ Example 103.

What is the minimum volume of water required to dissolve 1 g of calcium sulphate at 298. K_{sp} for $CaSO_4$ is 9.1×10^{-6}.

Solution: K_{sp} for $CaSO_4 = 9.1 \times 10^{-6}$

Let solubility of $CaSO_4$ be s.

$$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$$

$$[Ca^{2+}] = s\,, [SO_4^{2-}] = s$$

$$K_{sp} = [Ca^{2+}]\,[SO_4^{2-}]$$

$$= s \times s = s^2$$

$\therefore$ $$s^2 = K_{sp} = 9.1 \times 10^{-6}$$

$\therefore$ $$s = (9.1 \times 10^{-6})^{1/2} = 3.016 \times 10^{-3} \text{ mol } L^{-1}$$

1 mol of $CaSO_4 = 40 + 32 + 64 = 136$ g

Solubility $= 3.017 \times 10^{-3} \times 136 = 0.410$ g L^{-1}

0.41 g is dissolved in 1 L

1 g can be dissolved in $\frac{1}{0.41} = \mathbf{2.44\ L}$

❑ Example 104.

The solubility product of $Al(OH)_3$ is 2.7×10^{-11}. Calculate its solubility in gL^{-1} and also find out pH of this solution. (NCERT Exemplar Problem)

Solution: The solubility equilibrium is :

$$Al(OH)_3\,(s) \rightleftharpoons Al^{3+}\,(aq) + 3OH^-(aq)$$

Let the solubility of $Al(OH)_3$ be s mol L^{-1}, then

$$[Al^{3+}] = s, [OH^-] = 3s$$

$$K_{sp} = [Al^{3+}]\,[OH^-]^3 = s \times (3s)^3$$

$$= 27s^4$$

$\therefore$ $$27s^4 = 2.7 \times 10^{-11}$$

$$s^4 = \frac{2.7 \times 10^{-11}}{27} = 1 \times 10^{-12}$$

$\therefore$ $$s = (1 \times 10^{-12})^{1/4} = 1 \times 10^{-3} \text{ mol } L^{-1}$$

Molar mass of $Al(OH)_3 = 78$ g mol^{-1}

Solubility of $Al(OH)_3 = 1 \times 10^{-3} \times 78 = 7.8 \times 10^{-2}$ gL^{-1}

$$[OH^-] = 3s = 3 \times 1.0 \times 10^{-3} = 3.0 \times 10^{-3} \text{ mol } L^{-1}$$

$$pOH = -\log (3.0 \times 10^{-3}) = 2.5229$$

$\therefore$ $pH = 14 - pOH = 14 - 2.5229 = \mathbf{11.4771}$

Practice Problems

110. Calculate the solubility of $Mg(OH)_2$, if its solubility product is 5×10^{-12} at 298 K.

111. The solubility product of Ag_2CrO_4 is 1.9×10^{-12} at 300 K. What is its solubility ?

112. The solubility product of ferric hydroxide is 1.1×10^{-36} at 298 K. Calculate the solubility of ferric hydroxide in gram per litre. (Atomic mass, F = 56, O = 16)

113. The K_{sp} of CaF_2 at 298 K is 1.7×10^{-10}. Calculate its solubility in mol L^{-1}.

Answers to Practice Problems

110. 1.08×10^{-4} mol L^{-1}. **111.** 7.8×10^{-5} mol L^{-1}.

112. 4.8×10^{-8} g L^{-1}. **113.** 3.5×10^{-4} M.

Hints & Solutions on page 94

2. In Predicting the Precipitation in Reactions

Knowing the solubility product of a salt, it is possible to predict whether on mixing the solution of its ions, a precipitate will be formed or not. *For the precipitation to occur, its ionic product should exceed solubility product.* Therefore, to predict the precipitation reaction, we calculate the ionic product of the ions and find out whether it is greater than K_{sp} or not. Thus, if

Ionic product is greater than K_{sp} $\Rightarrow$ precipitation occurs

Ionic product is less than K_{sp} $\Rightarrow$ no precipitation occurs

Suppose we want to precipitate barium sulphate from a solution of barium chloride at a concentration of 0.5 M. The precipitation can be done by adding sulphuric acid in small amounts to the solution. Initially no precipitation occurs because the small amount of SO_4^{2-} is insufficient to make the ionic product, $[Ba^{2+}]\,[SO_4^{2-}]$ equal to solubility product of barium sulphate. When we have added sufficient amount of sulphuric acid so that the ionic product exceeds solubility product, barium sulphate would get precipitated. For example, the concentration of SO_4^{2-} ions necessary to cause precipitation of $BaSO_4$ ($K_{sp} = 1.5 \times 10^{-9}$) from a solution of 0.5 M $BaCl_2$ can be easily calculated as :

$$[Ba^{2+}] = [BaCl_2] = 0.5 \text{ M}$$

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}] = 1.5 \times 10^{-9}$$

$\therefore$ $$[SO_4^{2-}] = \frac{1.5 \times 10^{-9}}{0.5} = 3.0 \times 10^{-9} \text{ mol } L^{-1}$$

Thus, when the concentration of SO_4^{2-} ions is 3×10^{-9} mol L^{-1}, $BaSO_4$ would get precipitated.

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SOLVED EXAMPLES

Example 105.

The solubility product of $Fe(OH)_3$ is 1×10^{-36}. What is the minimum concentration of OH^- ions required to precipitate $Fe(OH)_3$ from a 0.001 M solution of $FeCl_3$?

Solution: K_{sp} for $Fe(OH)_3$ is :

$$K_{sp} = [Fe^{3+}]\,[OH^-]^3$$

Precipitation will occur when ionic product, $[Fe^{3+}]\,[OH^-]^3$ becomes greater than K_{sp}

$$[Fe^{3+}] = [FeCl_3] = 0.001 \text{ M}$$

The concentration of OH^- ions required to start the precipitation is :

$$[OH^-]^3 = \frac{K_{sp}}{[Fe^{3+}]} = \frac{1 \times 10^{-36}}{0.001} = 1 \times 10^{-33}$$

$$\therefore \quad [OH^-] = (1 \times 10^{-33})^{1/3} = 1 \times 10^{-11} \text{ mol L}^{-1}$$

Concentration of OH^- required to start precipitation of $Fe(OH)_3$ = **1×10^{-11} mol L^{-1}**

Example 106.

The solubility product of AgCl is 1.5×10^{-10}. Predict whether there will be any precipitation by mixing 50 ml of 0.01 M NaCl and 50 ml of 0.01 M $AgNO_3$ solution.

Solution: On mixing 50 ml of 0.01 M NaCl and 50 ml of 0.01 M $AgNO_3$ the total volume becomes 100 ml.

Therefore,

$$\text{Conc. of NaCl in 100 ml} = \frac{0.01 \times 50}{100} = 0.005 \text{ M}$$

$$\text{Conc. of } AgNO_3 \text{ in 100 ml} = \frac{0.01 \times 50}{100} = 0.005 \text{ M}$$

Now $\quad NaCl(aq) = Na^+(aq) + Cl^-(aq)$

and $\quad AgNO_3(aq) = Ag^+(aq) + NO_3^-(aq)$

$$[Cl^-] = [NaCl] = 0.005 \text{ M}$$

$$[Ag^+] = [AgNO_3] = 0.005 \text{ M}$$

$\therefore$ Ionic product of $[Ag^+]\,[Cl^-] = 0.005 \times 0.005$

$= \mathbf{2.5 \times 10^{-5}}$

Since ionic product is greater than its solubility product, **precipitation will occur.**

Example 107.

Calculate the molar solubility of $Ni(OH)_2$ in 0.10 M NaOH. The solubility product of $Ni(OH)_2$ is 2.0×10^{-15}.

Solution: Let the solubility of $Ni(OH)_2$ be s mol L^{-1}

$$Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$$

$$[Ni^{2+}] = s, [OH^-] = 2s$$

$$NaOH \longrightarrow Na^+ + OH^-$$

NaOH is strong base and it completely ionises and

$$[OH^-] = 0.10$$

$$\text{Total } [OH^-] = (2s + 0.10) \text{ mol L}^{-1}$$

$$K_{sp} = [Ni^{2+}]\,[OH^-]^2$$

$$= s(2s + 0.10)^2$$

As K_{sp} is small, $2s << 0.10$ so that $2s + 0.10 \approx 0.10$

$$K_{sp} = s \times (0.10)^2$$

or $\quad s\,(0.10)^2 = K_{sp} = 2.0 \times 10^{-15}$

$$s = \frac{2.0 \times 10^{-15}}{(0.10)^2} = 2.0 \times 10^{-13}$$

Molar solubility in 0.1 N NaOH = **2.0×10^{-13}M**

Example 108.

Equal volumes of 25.0 cm^3 of 5.0×10^{-2} M $Ba(NO_3)_2$ and 2×10^{-2} M NaF solution are mixed. Predict, whether precipitation of BaF_2 will be formed or not (K_{sp} of $BaF_2 = 1.7 \times 10^{-6}$ at 298 K).

Solution: The solubility equilibrium BaF_2 is :

$$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$$

On mixing 25.0 cm^3 of $Ba(NO_3)_2$ and 25.0 cm^3 of NaF, the solution becomes 25.0 + 25.0 = 50.0 cm^3. The new concentrations of $Ba(NO_3)_2$ and NaF are :

$$\text{Conc. of } Ba(NO_3)_2 = \frac{5.0 \times 10^{-2}}{50} \times 25 = 0.025 \text{ M}$$

$$\text{Conc. of NaF} = \frac{2.0 \times 10^{-2}}{50} \times 25 = 0.010 \text{ M}$$

Since $Ba(NO_3)_2$ ionises as :

$$Ba(NO_3)_2 = Ba^{2+} + 2NO_3^-$$

$$\therefore \quad [Ba^{2+}] = [Ba(NO_3)_2] = 0.025 \text{ M}$$

Since NaF ionises as

$$NaF = Na^+ + F^-$$

$$\therefore \quad [F^-] = [NaF] = 0.010 \text{ M}$$

$$\text{Now ionic product} = [Ba^{2+}]\,[F^-]^2$$

$$= (0.025)\,(0.010)^2$$

$$= 2.5 \times 10^{-6}$$

K_{sp} of salt = **1.7×10^{-6}**

As the product of ionic concentration of the ions of the salt solution is more than K_{sp}, the salt will be precipitated.

Example 109.

How many grams of potassium bromide (KBr) be added to 1 L of 0.05 M solution of silver nitrate just to start the precipitation of silver bromide ?

Solution: For AgBr, $K_{sp} = 5.0 \times 10^{-13}$

Precipitation of AgBr will occur when ionic product $[Ag^+]\,[Br^-]$ becomes larger than K_{sp}

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$

$$[Ag^+] = 0.05 \text{ M}$$

The concentration of Br^- required to start precipitation,

$$[Br^-] = \frac{K_{sp}}{[Ag^+]} = \frac{5.0 \times 10^{-13}}{0.05} = 1.0 \times 10^{-11}$$

$$\text{Now } [Br^-] = [KBr]$$

$$= 1.0 \times 10^{-11}$$

Molar mass of KBr = 120

$\therefore$ Amount of KBr required = $1.0 \times 10^{-11} \times 120$

$= \mathbf{1.20 \times 10^{-9}}$ **g**

Example 110.

What is the maximum concentration of equimolar solution of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no

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precipitation of iron sulphide? For iron sulphide, $K_{sp} = 6.3 \times 10^{-18}$.

Solution: Let the concentration of each of $FeSO_4$ and Na_2S is x mol L^{-1}. Then after mixing equal volumes :

$$[FeSO_4] = \frac{x}{2}\ M,\ [Na_2S] = \frac{x}{2} M$$

or $$[Fe^{2+}] = \frac{x}{2}\ M \text{ and } [S^{2-}] = \frac{x}{2}\ M$$

$$FeS \rightleftharpoons Fe^{2+} + S^{2-}$$

$$K_{sp} = [Fe^{2+}]\ [S^{2-}]$$

$$6.3 \times 10^{-18} = \frac{x}{2} \times \frac{x}{2}$$

or $$x^2 = 4 \times 6.3 \times 10^{-18} = 25.2 \times 10^{-18}$$

or $$x = \mathbf{5.02 \times 10^{-9}\ mol\ L^{-1}}.$$

Maximum concentration of $FeSO_4$ and Na_2S which will not precipitate iron sulphide = **5.02×10^{-9} mol L^{-1}.**

❑ Example 111.

The concentration of sulphide ion in 0.01 M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this solution is addd to 5 mL of 0.04 M solution of the following : $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$, in which of these solutions precipitation will take place?

Given Ksp, values : $FeS = 6.3 \times 10^{-18}$, $MnS = 2.5 \times 10^{-13}$, $ZnS = 1.6 \times 10^{-24}$, $CdS = 8.0 \times 10^{-27}$.

N.C.E.R.T.

Solution: Precipitation will occur in the solution for which ionic product is greater than K_{sp}. 10 mL of solution of H_2S is added to 5 mL solution of Fe^{2+}, Mn^{2+}, Zn^{2+} and Cd^{2+}. After mixing total volume becomes 10 + 5 = 15 mL

$$[S^{2-}] = \frac{1.0 \times 10^{-19} \times 10}{15} = 6.67 \times 10^{-20}\ M$$

$$[M^{2+}] = \frac{5}{15} \times 0.04 = 1.33 \times 10^{-2}\ M$$

$M^{2+} = Fe^{2+}, Mn^{2+}, Zn^{2+}$ or Cd^{2+}

Ionic product for each of these will be

$$[M^{2+}]\ [S^{2-}] = 1.33 \times 10^{-2} \times 6.67 \times 10^{-20}$$
$$= 8.87 \times 10^{-22}$$

The ionic product $[M^{2+}]\ [S^{2-}]$ is greater than K_{sp} of ZnS and CdS and, therefore, $ZnCl_2$ and $CdCl_2$ solution will be precipitated.

❑ Example 112.

Calculate the volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution. (K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$, atomic mass of Pb = 207).

Solution: The solubility equilibrium is :

$$PbCl_2\ (s) \rightleftharpoons Pb^{2+}\ (aq) + 2Cl^-\ (aq)$$

Let the solubility of $PbCl_2$ be s mol L^{-1}

$$[Pb^{2+}] = s, Cl^- = 2s$$

$$K_{sp} = [Pb^{2+}]\ [Cl^-]^2$$
$$= s \times (2s)^2 = 4s^3$$
$$4s^3 = 3.2 \times 10^{-8}$$
$$s^3 = \frac{3.2 \times 10^{-8}}{4} = 8 \times 10^{-9}$$
$$\therefore\ s = (8 \times 10^{-9})^{1/3} = 2.0 \times 10^{-3}\ mol\ L^{-1}$$

Solubility of $PbCl_2$ in gL^{-1} = $2.0 \times 10^{-3} \times 278$ (Molar mass = 278)
$= 556 \times 10^{-3}\ gL^{-1}$
$= 0.556$ g

To get saturated solution, 0.556 g of $PbCl_2$ is dissolved in 1L water.

0.1 g of $PbCl_2$ is dissolved in $\frac{0.1}{0.556}$ L = 0.1798 L water

∴ To make saturated solution, 0.1 g of $PbCl_2$ be dissolved in 0.1798 L or ≈ 0.2 L of water.

❑ Example 113.

The ionization constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}. How many times silver benzoate is more soluble in a buffer of pH 3.19 compared to its solubility in pure water ?

Solution: Let the solubility of C_6H_5COOAg in water is x mol L^{-1}

$$C_6H_5COOAg \rightleftharpoons C_6H_5COO + Ag^+$$

$[C_6H_5COO^-] = x$ mol L^{-1}, $[Ag^+] = x$ mol L^{-1}

$$K_{sp} = [C_6H_5COO^-]\ [Ag^+]$$
$$K_{sp} = x \times x = x^2$$
$$\therefore\ x^2 = K_{sp} \text{ or } x = \sqrt{K_{sp}}$$
$$\therefore\ x = \sqrt{2.5 \times 10^{-13}}$$
$$= 5.0 \times 10^{-7}\ mol\ L^{-1}$$

∴ Solubility of silver benzoate in water, $x = 5.0 \times 10^{-7}$ mol L^{-1}

pH of buffer = 3.19

or $-\log [H^+] = 3.19$

or $\log [H^+] = -3.19. = 4.81$

∴ $[H^+]$ = anti log (4.81) = 6.456×10^{-4}

$C_6H_5COO^-$ ions now combine with H^+ ions to form C_6H_6COOH but $[H^+]$ remains almost constant because, we have buffer solution.

Benzoic acid ionize as :

$$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$$

$$K_a = \frac{[C_6H_5COO^-]\ [H^+]}{[C_6H_5COOH]}$$

or $$\frac{[C_6H_5COOH]}{[C_6H_5COO^-]} = \frac{[H^+]}{K_a} = \frac{6.456 \times 10^{-4}}{6.46 \times 10^{-5}} = 10$$

Suppose solubility in buffer solution is y mol L^{-1}. Then most of the benzoate ions are converted into benzoic acid molecules (which remain almost ionized).

$$y = [Ag^+] = [C_6H_5COO^-] + [C_6H_5COOH]$$
$$= [C_6H_5COO^-] + 10\ [C_6H_5COO^-]$$
$$= 11\ [C_6H_5COO^-]$$

$$\therefore\ [C_6H_5COO^-] = \frac{y}{11}$$

But $$K_{sp} = [C_6H_5CO^-]\ [Ag^+]$$

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$$2.5 \times 10^{-13} = \frac{y}{11} \times y$$

or $$y^2 = 2.75 \times 10^{-12}$$

$$\therefore \quad y = (2.75 \times 10^{-12})^{\frac{1}{2}} = 1.66 \times 10^{-6}$$

Thus, $$\frac{y}{x} = \frac{1.66 \times 10^{-6}}{5.0 \times 10^{-7}} = 3.32$$

$\therefore$ Silver benzoate is 3.32 times more soluble in buffer.

Practice Problems

114. Can a precipitate of barium fluoride form when we mix 100 mL of 1.0×10^{-3} M $Ba(NO_3)_2$ (aq) and 200 mL of 1.0×10^{-3} M KF (aq). K_{sp} $(BaF_2) = 1.0 \times 10^{-6}$.

115. 50 ml of 0.04 M calcium nitrate solution is added to 150 ml of 0.08 M ammonium sulphate. Will a precipitate of calcium sulphate form or not ? $K_{sp} = 0.4 \times 10^{-5}$.

116. A solution containing 0.1 M Zn^{2+} and 0.01 M Cu^{2+} is saturated with H_2S. The S^{2-} concentration is 8.1×10^{-31} M. Will ZnS or CuS precipitate ? K_{sp} (ZnS) $= 3.0 \times 10^{-23}$ and K_{sp} (CuS) $= 8.0 \times 10^{-34}$.

117. What is the minimum concentration of sulphuric acid required to initiate the precipitation of $BaSO_4$ from a solution containing 7×10^{-8} mol L^{-1} of $BaCl_2$? [K_{sp} $(BaSO_4) = 1.4 \times 10^{-10}$].

118. Will a precipitate exist at equilibrium of ½ litre of a 4×10^{-2} M solution of NaOH and ½ litre of a solution of 2×10^{-3} M solution of $AlCl_3$ are mixed and diluted to 10^3 litres with water at room temperature ? K_{sp} of Al $(OH)_3 = 5 \times 10^{-33}$.

119. Equal volumes of 0.002 M solution of sodium iodate and copper chlorate are mixed together. Will it lead to precipitation of copper iodate ? For copper iodate $K_{sp} = 7.4 \times 10^{-4}$. ***N.C.E.R.T.***

Answers to Practice Problems

114. Ionic product $= 1.47 \times 10^{-4}$, precipitation can occur.

115. Ionic product $= 6 \times 10^{-4}$, yes.

116. CuS precipitates.

117. 2×10^{-3} mol L^{-1}

118. Yes, ionic product $= 8 \times 10^{-21}$

119. Ionic product $= 10^{-9}$, No precipitation will occur.

Hints & Solutions on page 94

COMMON ION EFFECT ON SOLUBILITY OF IONIC SALTS

We have learnt from Le-Chatelier principle that if we increase the concentration of any one of the ions, it would combine with the ion of its opposite charge and some of the salt will be precipitated till once again ionic product becomes equal to K_{sp} (*i.e.*, $Q_{sp} = K_{sp}$). Similarly, if the concentration of one of the ions is decreased, more salt will dissolve to increase the concentrations of both ions till once again ionic product becomes equal to K_{sp}. This is also applicable for soluble salts like sodium chloride except that because of higher concentrations we use their activities instead of their molarities in the expression for ionic product (Q_{sp}).This is also known as common ion effect.

The concepts of solubility product and common ion effect play an important role in the separation of basic radicals (cations) into different groups of qualitative analysis.

We have learnt that weak acids and weak bases slightly ionise in water and an equilibrium is established in their solutions. For example, consider the ionisation of a weak base NH_4OH as :

$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The ionisation constant for the base,

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

If solid NH_4Cl is added to the solution, the concentration of NH_4^+ ions increases. According to Le-Chatelier's principle, the equilibrium shifts to the left. As a result, the concentration of OH^- is considerably decreased and the weak base NH_4OH becomes even weaker in the presence of its salt.

$$NH_4OH \rightleftharpoons \boxed{NH_4^+} + OH^-$$
$$NH_4Cl \longrightarrow \boxed{NH_4^+} + Cl^-$$

Common ion

Similarly, the ionisation of a weak acid like CH_3COOH is suppressed by adding a salt of some acid (say CH_3COONa) due to common ion :

$$CH_3COOH \rightleftharpoons \boxed{CH_3COO^-} + H^+$$
$$CH_3COONa \longrightarrow \boxed{CH_3COO^-} + Na^+$$

Common ion

This phenomenon is called **common ion effect.** This may be defined as

the suppression of the degree of dissociation of a weak acid or a weak base by the addition of a strong electrolyte containing a common ion.

The common ion effect has been used to get sodium chloride of very high purity.

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Purification of Sodium Chloride

Sodium chloride obtained from sea-water or lakes is always impure. It can be purified on the basis of common ion effect as described below :

The saturated solution of impure sodium chloride is prepared by dissolving in minimum quantity of water. Then HCl gas is passed through this solution. The following equilibria are set up :

$$NaCl \rightleftharpoons Na^+ + \boxed{Cl^-}$$
$$HCl \longrightarrow H^+ + \boxed{Cl^-}$$

Common ion

Due to the presence of common chloride ions, the dissociation of sodium chloride is suppressed. This is known as common ion effect. The dissociation of sodium chloride is decreased to such an extent that the ionic product of NaCl exceeds its solubility product and it is thrown down as a precipitate.

On the other hand, the ionic products of the chlorides of cations (present as impurities) do not exceed and hence they remain in solution.

Use of common ion effect in qualitative analysis.

The common ion effect is generally employed in the qualitative analysis. Let us discuss some examples:

1. The cations of group II (Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, As^{3+}, Sb^{3+}, Sn^{2+}) are precipitated as their sulphides (such as CuS, PbS) by passing H_2S gas in the presence of hydrochloric acid. It has been found that the solubility products of sulphides of group II are lower than those of group IV sulphides (the radicals of this group also precipitate as sulphides). This means that lower concentration of S^{2-} ion, can easily precipitate group II radicals. Now hydrochloric acid is a strong electrolyte and gives a large number of H^+ ions. Due to the presence of common H^+ ions, the dissociation of H_2S is suppressed:

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$
$$HCl \longrightarrow H^+ + Cl^-$$

Therefore, the concentration of S^{2-} ion decreases. As a result, the decreased concentration of sulphide ions is sufficient to exceed the solubility products of sulphides of group II cations but not of group IV cations. Hence group IV radicals are not precipitated along with group II radicals.

2. The cations of group III are precipitated as their hydroxides by NH_4OH in the presence of NH_4Cl. Ammonium chloride is a strong electrolyte and gives a large number of NH_4^+ ions. Due to the common NH_4^+ ions, the degree of ionisation of NH_4OH is suppressed as :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

As a result, the concentration of OH^- ions gets reduced. However, this reduced concentration of OH^- ions is sufficient to precipitate the hydroxides of the cations of group III. This is because the solubility products of these hydroxides are low and the ionic product of metal ions concentration and OH^- ions concentration easily exceed solubility product. But the reduced concentration of OH^- ions is not sufficient to precipitate cations of succeeding groups because their solubility products are comparatively high.

3. The cations of group V are precipitated as their carbonates by the addition of $(NH_4)_2CO_3$ in the presence of NH_4Cl. As discussed earlier, due to the common NH_4^+ ions, the degree of ionisation of $(NH_4)_2CO_3$ is suppressed. Consequently, the concentration of carbonate decreases but it is sufficient to precipitate the carbonates of group V. This is so because the solubility products of group V cations are low as compared to carbonates of group VI cations particularly, Mg^{2+} ions.

Comparison of Solubility Product and Ionic Product

The main points of difference between solubility product and ionic product are given as :

Solubility product	Ionic product
1. It is the product of concentration of ions of the electrolyte, each raised to the power of their coefficients in the balanced chemical equation in a saturated solution.	1. It is the product of concentration of the ions of the electrolyte, each raised to the power of their coefficients in the balanced chemical equation in solution at any concentration.
2. It is applicable to only saturated solutions.	2. It is applicable to all types of solutions of any concentration.
3. It has a constant value for an electrolyte at a constant temperature.	3. Its value is not constant and varies with change in concentration.

Effect of pH on Solubility

The solubility of salts of weak acids increases at lower pH. This is because at lower pH, the concentration of the anion decreases due to its protonation. This increases the solubility of the salt till ionic product becomes equal to K_{sp}.

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Conceptual Questions 3

CONCEPTUAL QA

Q. 1. Which of the following combinations would result in the formation of a buffer solution ?
(*a*) $NH_4Cl + NH_3$ (*b*) $CH_3COOH + HCl$
(*c*) $CH_3COONa + CH_3COOH$ (*d*) $NH_3 + HCl$ in the molar ratio of 2 : 1
(*e*) HCl + NaOH

Ans. (*a*), (*c*), (*d*).

Q. 2. The K_{sp} values of two slightly soluble salts AB and PQ_2 are each equal to 4.0×10^{-18}. Which salt is more soluble ?

Ans. For AB salt,

$K_{sp} = [A^+]\,[B^-]$. If x is the solubility, then

$x^2 = 4.0 \times 10^{-18}$ or $x = 2.0 \times 10^{-9}$

For PQ_2 salt,

$K_{sp} = [P^{2+}]\,[Q^-]^2$

If y is the solubility, then

$4y^3 = K_{sp} = 4.0 \times 10^{-18}$ or $y = 1.0 \times 10^{-6}$

Since y is more than x, PQ_2 salt has more solubility.

Q.3. When a sample of AgCl was shaken with water, a solution containing 1.08×10^{-3} g/L of Ag^+ ion was produced. What is the solubility product of AgCl ?

Ans. $[Ag^+] = \dfrac{1.08 \times 10^{-3}}{108} = 1.0 \times 10^{-5}$ M

So $[Cl^-] = 1.0 \times 10^{-5}$ M

$K_{sp} = [Ag^+]\,[Cl^-] = 1.0 \times 10^{-5} \times 1.0 \times 10^{-5} = 1.0 \times 10^{-10}$

Q.4. Which of the following indicator/indicators may be used for the titration of a strong acid with a strong base ?

Phenolphthalein, methyl orange, methyl red.

Ans. All the three.

Q.5. What will be the pH of 0.1 M ammonium acetate solution ? $pK_a = pK_b = 4.74$.

Ans. For a salt of ammonium acetate,

$$pH = \frac{1}{2}\,pK_w + \frac{1}{2}\,pK_a - \frac{1}{2}\,pK_b$$

$$= \frac{1}{2}\,(14) + \frac{1}{2}\,(4.74) - \frac{1}{2}\,(4.74) = 7.$$

Q.6. The salt of strong acid and strong base does not undergo hydrolysis. Comment.

Ans. In this case, neither the cation nor the anion undergoes hydrolysis. Therefore, the solution remains neutral. For example, in the aqueous solution of NaCl, its ions Na^+ and Cl^- have no tendency to react with the H^+ or OH^- ions of water. This is because the possible products of such reaction are NaOH and HCl, which are themselves completely dissociated. As a result, there is no change in the concentration of H^+ and OH^- ions and hence the solution continues to remain neutral.

Q.7. Predict in which case, the degree of hydrolysis of independent of the concentration of the salt.
KCl, CH_3COONa, NH_4Cl, CH_3COONH_4 ***N.C.E.R.T.***

Ans. CH_3COONH_4

Q.8. The pK_{ind} of an indicator is 10.5 For which pH transition range is the indicator most suitable.

Ans. Most suitable pH range for the indicator is 9.5 – 11.5.

Q.9. The pH of an enzyme catalysed reaction has to be monitored between *p*H 7–8. What indicator should be used to monitor and control the pH of the reaction ? ***N.C.E.R.T.***

Ans. Bromothymol blue (6.0 – 7.5).

Q.10. Predict the acidic, basic or neutral nature of the solution of the following salts :
NaCl, KBr, NaCN, NH_4NO_3, $NaNO_2$ and KF.

Ans. NaCN, $NaNO_2$ and KF solution are basic
NaCl and KBr solutions are neutral
$NH_4\,NO_3$ solution is acidic.

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Advanced Level PROBLEMS *Accelerate Your Potential (for JEE Advance)*

Problem 8. The solubility of a salt of weak acid AB at pH 3 is $Y \times 10^{-3}$ mol L^{-1}. The solubility product (K_{sp}) of AB is 2×10^{-10} and ionization constant (K_a) of HB is 1×10^{-8}. What is the value of Y?

(JEE Advance 2018)

Solution Let solubility of AB is s so that s mol L^{-1} of A^+ and s mol L^{-1} of B^- are formed. Further, let x mol of B^- react with H^+ ions to form x mol of HB. Then $(s-x)$ mol of B^- will be present at equilibrium.

$$\underset{s}{AB(s)} \rightleftharpoons \underset{s}{A^+} + \underset{(s-x)}{B^-}$$

$$\underset{s-x}{B^-} + \underset{1\times10^{-3}}{H^+} \rightleftharpoons \underset{x}{HB}$$

[Since pH = 3, $[H^+] = 1 \times 10^{-3}$]

Now, $K_{sp} = s(s-x) = 2 \times 10^{-10}$ ...(*i*)

$$K_a = \frac{[B^-][H^+]}{[HB]} = 1 \times 10^{-8}$$

$$\frac{(s-x)\times10^{-3}}{x} = 1 \times 10^{-8}$$

or, $$\frac{s-x}{x} = 1 \times 10^{-5} \quad ...(ii)$$

Dividing eq. (*i*) by eq. (*ii*)

$$sx = 2 \times 10^{-5}$$

Now, $s(s-x) = 2 \times 10^{-10}$

$$s^2 - sx = 2 \times 10^{-10}$$

$$s^2 - 2 \times 10^{-5} = 2 \times 10^{-10}$$

$$s^2 = 2 \times 10^{-10} + 2 \times 10^{-5} \approx 2 \times 10^{-5}$$

$$s = \sqrt{2\times10^{-5}} = \sqrt{20} \times 10^{-6}$$

$$= 4.47 \times 10^{-3}$$

∴ Y = 4.47

Problem 9. What is the pH of a 1.0 M solution of acetic acid ? To what extent one litre of its solution be diluted so that the pH of the resulting solution will be twice the original value ? Given K_a for $CH_3COOH = 1.8 \times 10^{-5}$.

Solution For acetic acid

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$[H_3O^+] = \sqrt{K_a.C} = \sqrt{1.8 \times 10^{-5} \times 1}$$

$$= 4.24 \times 10^{-3}$$

$$pH = -\log(4.2 \times 10^{-3}) = 2.372$$

∴ The pH of the diluted solution = 2 × 2.372 = 4.744

$$pH = 4.744$$

$$-\log[H_3O^+] = 4.744$$

$$[H_3O^+] = 1.80 \times 10^{-5}$$

Let the new concentration of CH_3COOH in the diluted solution be c molL^{-1}.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

At equ. $c - 1.8 \times 10^{-5}$ 1.8×10^{-5} 1.8×10^{-5}

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$= \frac{(1.8\times10^{-5})(1.8\times10^{-5})}{(c-1.8\times10^{-5})} = 1.8\times10^{-5}$$

or $$\frac{(1.8\times10^{-5})}{c-1.8\times10^{-5}} = 1$$

or $c - 1.8 \times 10^{-5} = 1.8 \times 10^{-5}$

or $c = 1.8 \times 10^{-5} + 1.8 \times 10^{-5} = 3.6 \times 10^{-5}$

The number of moles of CH_3COOH before and after dilution will be the same. Let the volume of diluted solution be V litre.

∴ Moles of CH_3COOH = Molarity × Volume of solution in litres

$$3.6 \times 10^{-5} \times V = 1.0 \times 1$$

or $$V = \frac{1}{3.6\times10^{-5}} = 2.78 \times 10^4 L$$

∴ 1L of 1 M CH_3COOH solution should be diluted to 2.78×10^4L

Problem 10. The pH of a solution of $B(OH)_2$ is 10.6. Calculate its solubility and solubility product.

Solution

$$pH = 10.6$$

$$pH + pOH = 14$$

or $$pOH = 14 - 10.6 = 3.4$$

$$-\log[OH^-] = 3.4$$

or $$\log[OH^-] = -3.4 = \bar{4}.6$$

$$[OH^-] = 3.98 \times 10^{-4} \text{ mol } L^{-1}$$

Now, $B(OH)_2$ dissociates as :

$$B(OH)_2 \rightleftharpoons B^+ + 2OH^-$$

It is clear that 1 mol of $B(OH)_2$ gives 2 mol of OH^-

$$\text{Solubility of } B(OH)_2 = \frac{1}{2}[OH^-]$$

$$= \frac{1}{2} \times (3.98 \times 10^{-4})$$

$$= 1.99 \times 10^{-4} \text{ mol } L^{-1}$$

Now, $K_{sp} = [B^+][OH^-]^2$

∴ $[B^+] = 1.99 \times 10^{-4}$ mol L^{-1},

$[OH^-] = 3.98 \times 10^{-4}$ mol L^{-1}

∴ $K_{sp} = (1.99 \times 10^{-4}) \times (3.98 \times 10^{-4})^2$

$= \mathbf{3.15 \times 10^{-11}}$.

Problem 11. A sample of AgCl was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- per litre. Calculate the solubility product of AgCl.

(K_{sp} of $Ag_2CO_3 = 8.2 \times 10^{-12}$)

Solution

$$Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$$

$$K_{sp}(Ag_2CO_3) = [Ag^+]^2[CO_3^{2-}]$$

1.5 M Na_2CO_3 gives, $[CO_3^{2-}] = 1.5$ M

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Concentration of Ag^+ ion in solution,

$$[Ag^+] = \left(\frac{K_{sp}\,(Ag_2CO_3)}{[CO_3^{2-}]}\right)^{\frac{1}{2}} =$$

$$\left(\frac{8.2\times10^{-12}}{1.5}\right)^{\frac{1}{2}} = 2.34\times10^{-6}\ M$$

$$[Cl^-] = \frac{0.0026\ gL^{-1}}{35.5\ g\ mol^{-1}} = 7.32\times10^{-5}\ M$$

$$K_{sp} = [Ag^+]\,[Cl^-] = (2.34\times10^{-6})\,(7.32\times10^{-5}) = \mathbf{1.71\times10^{-10}}.$$

Problem 12. **An acid type indicator, HIn differs in colour from its conjugate base $[In^-]$. The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change ($K_a = 1.0\times10^{-5}$)?**

Solution

$$HIn \rightleftharpoons H^+ + In^-$$

$$K_a = \frac{[H^+][In^-]}{[HIn]} \text{ or } [H^+] = K_a\frac{[HIn]}{[In^-]}$$

When $\frac{[In^-]}{[HIn]} = 10$, $[H^+] = 10^{-5}\times\frac{1}{10} = 10^{-6}$

or $pH = -\log[H^+] = -\log(10^{-6}) = 6$

When $\frac{[In^-]}{[HIn]} = 0.1$, $[H^+] = 10^{-5}\times10 = 10^{-4}$

or $pH = -\log[H^+] = -\log(10^{-4}) = 4$

∴ Minimum pH change = 2

Problem 13. **Calculate the pH at which $Mg(OH)_2$ begins to precipitate from a solution containing 0.1 M Mg^{2+} ions. K_{sp} for $Mg(OH)_2 = 1.0\times10^{-11}$.**

Solution $[Mg^{2+}] = 0.1$ M, $K_{sp} = 1.0\times10^{-11}$

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$1.0\times10^{-11} = (0.1)\,[OH^-]^2$$

or $$[OH^-]^2 = \frac{1.0\times10^{-11}}{0.1} = 10^{-10},\ [OH^-] = 10^{-5}\ M$$

Now, $$[H_3O^+][OH^-] = K_w = 10^{-14}$$

$$[H_3O^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{10^{-5}} = 10^{-9}\ M$$

$$pH = -\log[H_3O^+] = -\log(10^{-9}) = \mathbf{9}.$$

Problem 14. **The buffers of (X) and (Y) of *p*H 4.0 and 6.0 respectively are prepared from acid HA and the salt NaA. Both the buffers are 0.50 M in HA. What would be the *p*H of the solution obtained by mixing equal volumes of the two buffers ? ($K_{HA} = 1.0\times10^{-5}$)**

Solution

$$K_{HA} = 1.0\times10^{-5}$$

∴ $$pK_a = -\log(1.0\times10^{-5}) = 5.0$$

Determination of conc. of salt in buffer X

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$$4.0 = 5.0 + \log\frac{[Salt]}{0.5}$$

$$\log\frac{[Salt]}{0.5} = -1$$

$$\frac{[Salt]}{0.5} = 10^{-1}$$

$$[Salt] = 0.5\times10^{-1} = 0.05\ M$$

Determination of conc. of salt in buffer Y

$$6.0 = 5.0 + \log\frac{[Salt]}{0.5}$$

$$\log\frac{[Salt]}{0.5} = 1.0$$

$$\frac{[Salt]}{0.5} = 10$$

∴ $$[Salt] = 10\times0.5 = 5.0\ M$$

Conc. of salt in the mixture,

$$[Salt]_{mix} = \frac{0.05+5.0}{2} = 2.525\ M$$

$$pH = pK_a + \log\frac{[Salt]}{[Acid]} = 5.0 + \log\frac{2.525}{0.5} = 5.0 + 0.70 = \mathbf{5.7}.$$

Problem 15. **How many times of the acetic acid concentration, acetate salt should be added to a given acetic acid solution to obtain a solution of pH = 7.0 (K_a for $CH_3COOH = 1.8\times10^{-5}$).**

Solution Let the concentration of acetate salt be x times the concentration of acetic acid solution to get pH = 7. Then

$$[CH_3COO^-] = x\times[CH_3COOH]$$

or $$\frac{[CH_3COO^-]}{[CH_3COOH]} = x$$

For acidic buffer, $$pH = pK_a + \log\frac{[Salt]}{Acid}$$

or $$7 = -\log(1.8\times10^{-5}) + \log x$$

or $$7 = 4.76 + \log x$$

or $$\log x = 2.24$$

or $$x = 173.8 \text{ times}.$$

Problem 16. **If 50 mL of solution containing 0.001 mol Ag^+ ion is mixed with 50 mL of 0.10 M HCl solution, how much Ag^+ ions remain in the solution? (K_{sp} of AgCl = 1×10^{-10}).**

Solution Moles of Cl^- ions present in 50 mL of 0.10 M HCl

$$= \frac{0.10}{1000}\times50 = 0.005\ mol$$

Let x mol of Ag^+ ion remains in solution.

Moles of Ag^+ ion precipitated = $0.001 - x \approx 0.001$ mol (x is very small)

Moles of Cl^- ion precipitated = 0.001 mol

Moles of Cl^- left = 0.005 – 0.001 = 0.004 mol

Total volume of solution = 50 + 50 = 100 mL

$$[Cl^-] = \frac{0.004}{100}\times1000 = 0.040\ M$$

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$K_{sp} = [Ag^+][Cl^-] = [Ag^+] \times 0.040 = 1 \times 10^{-10}$

$\therefore \quad [Ag^+] = \frac{1\times10^{-10}}{0.04} = 2.5 \times 10^{-9}$

Moles of Ag^+ ions remaining in 100 mL

$= \frac{2.5\times10^{-9}}{1000} \times 100$

$= 2.5 \times 10^{-10}$ mol

Problem 17. What will be the resultant pH when 200 ml of an aqueous solution of HCl (*p*H = 2) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12.0)?

Solution pH of HCl = 2 $\therefore [H_3O^+] = 10^{-2}$ M

Moles of H^+ ions in 200 ml of 10^{-2} M HCl

$= \frac{10^{-2}}{1000} \times 200 = 2 \times 10^{-3}$

pH of NaOH = 12

$\therefore \quad [H^+] = 10^{-12}$ or $[OH^-] = 10^{-2}$

Moles of OH^- ions in 300 ml of 10^{-2} M NaOH

$= \frac{10^{-2}}{1000} \times 300 = 3 \times 10^{-3}$

2×10^{-3} mol of H^+ will be neutralised with 2×10^{-3} mol of OH^- ions

Moles of OH^- left in 500 ml of solution after mixing

$= 3 \times 10^{-3} - 2 \times 10^{-3}$

$= 1 \times 10^{-3}$

Molar concentration of OH^- in resulting solution

$= \frac{1\times10^{-3}}{500} \times 1000$

$= 2 \times 10^{-3}$ M

pOH $= -\log(2 \times 10^{-3})$

$= 2.698$

$\therefore \quad$ pH $= 14 - 2.698 =$ **11.302**

Solution File

Hints & Solutions for Practice Problems

1. $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

$= \frac{(1.2\times10^{-2})^2}{(1.5\times10^{-2})\times(3.0\times10^{-2})^3}$

$=$ **3.56×10^2.**

2. $K_c = \frac{[HBr]^2}{[H_2][Br_2]}$

$[H_2] = \frac{2.5\times10^{-3}}{10} = 2.5 \times 10^{-4}$,

$[Br_2] = \frac{2.8\times10^{-3}}{10} = 2.8 \times 10^{-4}$

$[HBr] = \frac{0.150}{10} = 1.5 \times 10^{-2}$

$K_c = \frac{(1.5\times10^{-2})^2}{(2.5\times10^{-4})(2.8\times10^{-4})}$

$=$ **3.21×10^3**

3. $K_p = \frac{(p_{NO})^2\, p_{(Cl_2)}}{(p_{NOCl})^2}$

$= \frac{(0.11)^2\times(0.84)}{(0.75)^2}$

$=$ **0.0181**

4. $K = \frac{[NO_2]^2}{[N_2][O_2]}$

$[NO_2] = \frac{0.10}{1.5}$, $[N_2] = \frac{5.0}{1.5}$, $[O_2] = \frac{7.0}{1.5}$

$K = \frac{\left(\frac{0.10}{1.5}\right)^2}{\left(\frac{5.0}{1.5}\right)\left(\frac{7.0}{1.5}\right)^2} =$ **6.12×10^{-5}**

6. $K_c = K_p \left(\frac{1}{RT}\right)^{\Delta n_g}$

$\Delta n = 2 - 1 = 1$

$K_c = 0.157 \times \left(\frac{1}{0.0821\times300}\right)^1$

$=$ **6.37×10^{-3} mol L^{-1}**

7. $K_p = K_c (RT)^{\Delta n_g}$

$\Delta n = 2 - (1 + 3) = -2$

$K_p = 6.05 \times 10^{-2} \times (0.0821 \times 800)^{-2}$

$=$ **1.40×10^{-5} atm^{-2}**

10. $K = \frac{[ICl(g)]^2}{[I_2(g)][Cl_2(g)]} = 640$

$2ICl(g) \rightleftharpoons I_2(g) + Cl_2(g)$

$K' = \frac{[I_2(g)][Cl_2(g)]}{[ICl(g)]^2} = \frac{1}{K} = \frac{1}{640}$

$=$ **1.56×10^{-3}.**

11. $K_p = \frac{(p_{NH_3})^2}{(p_{N_2})\times(p_{H_2})^3}$, $K_p = 41$

(*i*) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

$K_p' = \frac{1}{K_p} = \frac{1}{41} =$ **0.024**

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(*ii*) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$

$$K_p'' = \frac{(p_{NH_3})}{(p_{N_2})^{1/2}(p_{H_2})^{3/2}} = (41)^{1/2} = \mathbf{6.4}$$

(*iii*) $2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$

$$K_p''' = \frac{(p_{NH_3})^4}{(p_{N_2})^2(p_{H_2})^6} = (41)^2 = \mathbf{1681}$$

12. $K_c = K_p(RT)^{-\Delta n_g}$

$\Delta n_g = (2+1) - 2 = 1$

$K_c = 1.8 \times 10^{-2} \times (0.083 \times 500)^{-1}$

$= \mathbf{4.33 \times 10^{-4}}$.

13. For the reaction, $2A(g) + 2B_2(g) \rightleftharpoons 2AB_2(g)$

$$K_p = \frac{(p_{AB_2})^2}{(p_A)^2.p(B_2)^2} = 4.0$$

(*a*) $2AB_2(g) \rightleftharpoons 2A(g) + 2B_2(g)$

$$K_p' = \frac{(p_A)^2(p_{B_2})^2}{(p_{AB_2})^2} = \frac{1}{K_p} = \frac{1}{4.0}$$

$= \mathbf{0.25}$

(*b*) $A(g) + B_2(g) \rightleftharpoons AB_2(g)$

$$K_p'' = \frac{(p_{AB_2})^2}{p_A.p_{B_2}} = \sqrt{K_p} = \sqrt{4.0}$$

$= \mathbf{2.0}$.

14. $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ $K_1 = \frac{[NO_2]^2}{[NO]^2[O_2]}$

$4NO_2(g) \rightleftharpoons 2NO(g) + 2O_2(g)$

$$K_2 = \frac{[NO]^4[O_2]^2}{[NO_2]^4}$$

$$K_2 = \frac{1}{K_1^2}$$

15. $2SO_2 + O_2 \rightleftharpoons 2SO_3$

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = 256$$

For the reaction

$$SO_3 \rightleftharpoons SO_2 + \frac{1}{2}O_2$$

$$K' = \frac{[SO_2][O_2]^{1/2}}{[SO_3]}$$

Now, $\frac{1}{K'^2} = K$ or $K' = \frac{1}{\sqrt{K}} = \frac{1}{\sqrt{256}}$

$K = \frac{1}{16} = \mathbf{6.25 \times 10^{-2}}$.

16. The equilibrium reaction is

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

Initial.conc.	1	1	0	0
Equi.conc.	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$

Let the volume of the vessel is 1L, then equilibrium constant :

$$K = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$= \frac{\frac{2}{3} \times \frac{2}{3}}{\frac{1}{3} \times \frac{1}{3}} = \mathbf{4}$$

17. Amount of HI decomposed $= \frac{2 \times 22}{100} = 0.44$ mol

	$2HI \rightleftharpoons$	H_2	+	I_2
Initial conc.	2	0		0
Equi. conc.	$(2 - 0.44)$	0.22		0.22
	$= 1.56$			

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.22 \times 0.22}{(1.56)^2}$$

$= \mathbf{0.0199}$.

18. $H_2 + I_2 \rightleftharpoons 2HI$

Let us suppose that x mol/litre of hydrogen react. This will react with x moles of I_2 and form $2x$ mol of HI. Then the concentrations are :

	H_2	+	I_2	$\rightleftharpoons$	2HI
Initial conc.	1		1		0
Equi. conc.	$(1-x)$		$(1-x)$		$2x$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} \text{ or } 66.5 = \frac{(2x)^2}{(1-x)(1-x)} = \left(\frac{2x}{1-x}\right)^2$$

Taking square root on both sides

$$8.15 = \frac{2x}{1-x}$$

or $2x = 8.15 - 8.15x$

or $10.15\,x = 8.15$

or $x = \frac{8.15}{10.15} = 0.803$

$\therefore$ $[H_2] = 1 - x = 1.0 - 0.803$

$= 0.197$,

$[I_2] = 1 - x$

$= 0.197$

$[HI] = 2x = 0.803 \times 2 = \mathbf{1.606}$.

19. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

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$$Q = \frac{(0.50)^2}{(3.0)\times(2.0)^3} = \mathbf{0.0104}$$

Reaction will proceed to form more products i.e., in the forward direction.

20. $CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$

$$Q = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2}$$

(*i*) $[CH_4] = 1.07$ M, $[H_2S] = 1.20$ M, $[CS_2] = 0.90$ M, $[H_2] = 1.78$ M

$$Q = \frac{(0.90)\times(1.78)^4}{(1.07)\times(1.20)^2} = \mathbf{5.86}$$

Reaction will proceed in the backward direction.

(*ii*) $[CH_4] = 1.45$ M, $[H_2S] = 1.29$ M, $[CS_2] = 1.25$ M, $[H_2] = 1.75$ M

$$Q = \frac{(1.25)\times(1.75)^4}{(1.45)\times(1.29)^2} = \mathbf{4.86}$$

Reaction will proceed in the backward direction.

21. Initial concentration of each gas = 1 mol

Let number of moles of NO_2 reacting at equilibrium = x

Then, equilibrium concentrations are :

	$SO_2(g)$	+ $NO_2(g)$	$\rightleftharpoons$ $SO_3(g)$	+ $NO(g)$
Initial conc.	1	1	1	1
Equi. conc.	$(1-x)$	$(1-x)$	$(1+x)$	$(1+x)$

$$K_c = \frac{[SO_3][NO]}{[SO_2][NO_2]}$$

or $\dfrac{(1+x)(1+x)}{(1-x)(1-x)} = 16$

or $\left(\dfrac{1+x}{1-x}\right)^2 = 16$ or $\dfrac{1+x}{1-x} = 4$

or $1 + x = 4 - 4x$

or $5x = 3 \quad x = 3/5 = 0.6$

∴ Concentration at equilibrium

$[NO] = 1 + x = 1 + 0.6 = \mathbf{1.6\ mol.}$

$[NO_2] = 1 - x = 1 - 0.6 = \mathbf{0.4\ mol.}$

22. Initial concentration of $PCl_5 = 1.5$ mol

No. of moles of PCl_5 dissociated = $\dfrac{1.5\times35}{100} = 0.525$

Now, 1 mole of PCl_5 on dissociation gives 1 mol of PCl_3 and 1 mol of Cl_2. 0.525 mol of PCl_5 on dissociation will give 0.525 mol of PCl_3 and 0.525 mol of Cl_2.

Volume of the flask = 4L

Molar conc. at equilibrium are

	$PCl_5(g)$	$\rightleftharpoons$ $PCl_3(g)$	+ $Cl_2(g)$
Initial conc.	1.5/4	0	0
Equi. conc.	$\dfrac{1.5-0.525}{4}$	$\dfrac{0.525}{4}$	$\dfrac{0.525}{4}$
	= 0.975/4		

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.525/4)(0.525/4)}{(0.975/4)} = \mathbf{0.071}$$

23. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$p_{N_2} = 0.80$ atm $\quad p_{H_2} = 0.40$ atm

$p_{NH_3} = 2.80 - (0.80 + 0.40) = 1.60$ atm

Now, $K_p = \dfrac{(p_{NH_3})^2}{p_{N_2}\times(p_{H_2})^3}$

or $\dfrac{(1.60)^2}{0.80\times(0.40)^3}$

$= 50\ \text{atm}^{-2}$

Now $K_c = K_p(RT)^{-\Delta n}$

$\Delta_n = 2 - (1 + 3) = -2$

∴ $K_c = 50\ (\text{atm}^{-2}) \times (0.082\ \text{atm L K}^{-1}\ \text{mol}^{-1}\ 400\ \text{K})^2$

$= \mathbf{53.8 \times 10^3\ mol^{-2}\ L^2.}$

24.

	$2SO_2(g)$	+ $O_2(g)$	$\rightleftharpoons$ $2SO_3(g)$
Initial pressure	0	2 atm	1 atm

Since volume of the vessel remains constant, so that the partial pressures are proportional to moles. Let us assume that at equilibrium $2x$ moles of SO_3 have decomposed to give $2x$ moles of $SO_2(g)$ and x moles of O_2. Thus at equilibrium,

	$2SO_2$	+ O_2	$\rightleftharpoons$ $2SO_3$
Equi pressure	$2x$ atm	$(2 + x)$ atm	$(1 - 2x)$ atm

$$K_p = \frac{\left[p_{(SO_3)}\right]^2}{\left[p_{(SO_2)}\right]^2\left[p_{O_2}\right]} = 900$$

or $\dfrac{(1-2x)^2}{(2x)^2(2+x)} = 900$

Since x is very small assuming $1 - 2x \approx 1$, $2 + x \approx 2$ and solving for x

$x = 0.0118$

$p_{SO_2} = 2x = 2 \times 0.0118 = \mathbf{0.0236\ atm}$

$p_{O_2} = 2 + x = 2 + 0.0118 = \mathbf{2.0118\ atm}$

$p_{SO_3} = 1 - 2x = 1 - 2 \times 0.0118 = \mathbf{0.976\ atm}$

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25. The reaction is

$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

Let the decrease in pressure of CO_2 due to reaction be p atm.

Increase in pressure due to formation of CO = $2p$ atm

Pressure of CO_2 left = $(0.5 - p)$ atm.

Pressure of CO = $2p$ atm.

Total pressure = $0.5 - p + 2p = (0.5 + p)$ atm.

$\therefore \quad 0.5 + p = 0.8$ or $p = 0.3$

$\therefore$ At equilibrium, $p_{CO_2} = 0.5 - 0.3 = 0.2$ atm

$$2p_{CO} = 0.3 \times 2 = 0.6 \text{ atm}$$

$$K = \frac{(p_{CO})^2}{p_{CO_2}} = \frac{(0.6)^2}{0.2} = \mathbf{1.8 \text{ atm.}}$$

26. *(i) Calculation of K_p*

When total pressure is 1 atm.

Press. at equilibrium $\quad N_2O_4 \rightleftharpoons 2NO_2$

$\qquad\qquad\qquad\qquad\quad 0.7 \qquad\quad 0.3$

$$K_p = \frac{\left[p_{(NO_2)}\right]^2}{p_{(N_2O_4)}} = \frac{(0.3)^2}{0.7} = 0.1286 \text{ atm.}$$

Let the degree of dissociation of $N_2O_4 = \alpha$

$\qquad N_2O_4 \rightleftharpoons 2NO_2$

Moles at equi. $1 - \alpha \qquad 2\alpha$

Total number of moles = $1 - \alpha + 2\alpha = 1 + \alpha$

$$p_{(NO_2)} = \frac{2\alpha}{1+\alpha} \times 10 \qquad (P = 10)$$

$$p_{(N_2O_4)} = \frac{1-\alpha}{1+\alpha} \times 10$$

$$K_p = \frac{\left[p_{(NO_2)}\right]^2}{p_{(N_2O_4)}} = \frac{\left(\frac{2\alpha}{1+\alpha}\times 10\right)^2}{\frac{1-\alpha}{1+\alpha}\times 10} = \frac{4\alpha^2}{1-\alpha^2}\times 10$$

Now, α is very small so that $1 - \alpha^2 \approx 1$

$$\therefore 0.1286 = \frac{4\alpha^2}{1} \times 10 \text{ or } \alpha^2 = \frac{0.1286}{40} = 0.0032$$

$$\therefore \quad \alpha = 0.057$$

$$p_{(N_2O_4)} = \frac{1-0.057}{1+0.057}\times 10 = \mathbf{8.92 \text{ atm}}$$

$$p_{(NO_2)} = \frac{2\times 0.057}{1+0.057}\times 10 = \mathbf{1.08 \text{ atm}}$$

27. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Total pressure of the mixture = 10 atm

$$p_{N_2} + p_{H_2} + p_{NH_3} = 10 \text{ atm}$$

Now, $p_{NH_3} = 52\%$ or $= \frac{52\times 10}{100} = 5.2$ atm

$\therefore p_{N_2} + p_{H_2} = 10 - 5.2 = 4.8$ atm

Since N_2 and H_2 are present in the ratio of 1 : 3

$$p_{N_2} = \frac{1}{4} \times 4.8 = 1.2 \text{ atm}$$

$$p_{H_2} = \frac{3}{4} \times 4.8 = 3.6 \text{ atm}$$

$$K_p = \frac{\left(p_{NH_3}\right)^2}{\left(p_{N_2}\right)\left(p_{H_2}\right)^3} = \frac{(5.2)^2}{(1.2)(3.6)^3} = \mathbf{0.4830}$$

$K_p = K_c (RT)^{\Delta n_g}$

$\Delta n = 2 - (1 + 3) = -2$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{0.4830}{(0.082\times 480)^{-2}} = \mathbf{750.1.}$$

28. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Let concentration of PCl_3 and Cl_2 at equilibrium be x mol L^{-1}.

$$[PCl_5] = 0.05$$

$$K_c = 8.3 \times 10^{-3}$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$8.3 \times 10^{-3} = \frac{x \times x}{0.05}$$

$$x = 2.04 \times 10^{-2} \text{ mol L}^{-1}$$

$$\therefore \quad [PCl_3] = \mathbf{2.04 \times 10^{-2} \text{ mol L}^{-1}}$$

$$[Cl_2] = \mathbf{2.04 \times 10^{-2} \text{ mol L}^{-1}.}$$

29. $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

Initially 0.5 atm of NH_3 was present and NH_4HS (*s*) is added to the flask. Let at equilibrium, NH_4HS dissociates to give '*a*' moles of NH_3 and '*a*' moles of H_2S.

$$\therefore \quad p_{NH_3} = (0.5 + a)$$

$$p_{H_2S} = a$$

$$K_p = p_{NH_3} \times p_{H_2S}$$

$$0.11 = (0.5 + a) \times (a)$$

$$a^2 + 0.5a - 0.11 = 0$$

Solving we get, $\quad a = 0.1653$ atm

$$\therefore \quad p_{NH_3} = \mathbf{0.1653 + 0.5 = 0.6653 \text{ atm}}$$

$$p_{H_2S} = \mathbf{0.1653 \text{ atm}}$$

30. $S_8(g) \rightleftharpoons 4S_2(g)$

Initial pressure $\quad 1 \qquad 0$

Pressure at equil. $\quad 1 - \alpha \qquad 4\alpha$

Since at equilibrium $\alpha = 29\% = 0.29$

$$\therefore \quad p_{S_8} = 1 - \alpha = 1 - 0.29 = 0.71$$

$$p_{S_2} = 4\alpha = 4 \times 0.29 = 1.16$$

$$K_p = \frac{\left[p_{S_2}\right]^4}{p_{S_8}} = \frac{(1.16)^4}{0.71} = \mathbf{2.55 \text{ atm}^3.}$$

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31. Let after dissociation the decrease in pressure of XY_2 at equilibrium is p mm of Hg

$$XY_2(g) \rightleftharpoons XY(g) + Y(g)$$

Initial	500 mm	0	0
At equi.	(500–p)mm	p mm	p mm

Total pressure at equilibrium = 500–p + p + p = (500 + p) mm

$\therefore$ 500 + p = 700 (given) or p = 200 mm

Hence, at equilibrium, $p(XY_2)$ = 500 – 200 = 300 mm

p (XY) = 200 mm, p(Y) = 200 mm

$$K_p = \frac{p(XY) \times p(Y)}{p(XY_2)}$$

$$= \frac{200 \times 200}{300} = \mathbf{133.3\ mm}$$

32. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

Initial conc. of $PCl_5 = \frac{1.50}{0.500} = 3.0$ mol L^{-1}

Suppose amount of PCl_5 dissociated is x so that at equilibrium :

$$[PCl_5] = 3.0 - x,\ [PCl_3] = x,\ [Cl_2] = x$$

$$K_c = \frac{x \times x}{3.0 - x}$$

$$1.80 = \frac{x^2}{3.0 - x} \text{ or } 5.40 - 1.80\,x = x^2$$

Solving for x, we get

$$x = 1.59 \text{ and } -3.39$$

Ignoring x = – 3.39; we get

$$\mathbf{[PCl_5]} = 3.00 - 1.59 = \mathbf{1.41\ mol\ L^{-1}},$$

$$\mathbf{[PCl_3]} = \mathbf{1.59\ mol\ L^{-1}}$$

$$\mathbf{[Cl_2]} = \mathbf{1.59\ mol\ L^{-1}}$$

33. K_c (reverse reaction)

$$= \frac{1}{6.3 \times 10^{14}} = \mathbf{1.587 \times 10^{-15}}$$

34.

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{\left(\frac{8.13}{20}\right)^2}{\left(\frac{1.57}{20}\right)\left(\frac{1.92}{20}\right)^3} = 2.38 \times 10^3$$

So, reaction is not at equilibrium. Reaction will proceed in the direction of reactants i.e., reverse reaction.

35.

$$Q_c = \frac{[B][C]}{[A]^2}$$

$$= \frac{(3\times10^{-4})\times(3\times10^{-4})}{(3\times10^{-4})^2} = 1$$

Since $Q_c > K_c$ so, the reaction will proceed in the reverse direction.

36.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

	3.0	0	0
Initial conc.	3–x	x	x

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$1.8 = \frac{x \times x}{3 - x} = \frac{x^2}{3 - x}$$

Solving for x, we get x = 1.59

$[PCl_5]$ = 3–1.59 = 1.41 M, $[PCl_3] = [Cl_2]$ = 1.59 M

37.

$$2HI(g) \rightleftharpoons H_2(g) + I_2$$

At equi.	0.5	x	x

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{54.8}$$

$$\frac{x^2}{(0.5)^2} = \frac{1}{54.8}$$

$$x^2 = \frac{0.25}{54.8} = 4.56 \times 10^{-3}.$$

x = 0.068

$[H_2] = [I_2]$ = **0.068 mol L^{-1}**

38.

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

Initial conc.	4.0 atm	0	0
At equi.	4 – p	p	p

$$K_p = \frac{p \times p}{4 - p} = 0.04$$

$$p^2 = 0.16 - 0.04\,p$$

Solving for p,we get p = 0.38

$\therefore$ Conc of C_2H_6 at eq. = 4 – 0.38 = **3.62 atm**

39.

$$\log K = -\frac{\Delta G^\circ}{2.303\,RT}$$

$$= -\frac{-142\times10^3}{2.303\times8.314\times300}$$

$$= 24.72$$

$\therefore$ K = **5.25×10^{24}**

40. $\Delta G^\circ = -2.303\,RT \log K$

$= -2.303 \times 8.314 \times 298 \times \log 1.55 \times 10^{15}$

= **– 86.7 kJ mol^{-1}**

41.

$$\log K = -\frac{\Delta G^\circ}{2.303\,RT}$$

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$$= -\frac{-474.78\times10^3}{2.303\times8.314\times298}$$

$$= \mathbf{83.21}$$

42. $\Delta G^\circ = 2.303\ RT \log K$

$= -2.303 \times 8.314 \times 298 \times \log(2\times10^7)$

$= \mathbf{-12.023\ kJ}$

61. $\therefore\ -\log[H_3O^+] = 7.4$

$\log[H_3O^+] = -7.4$

or $[H_3O^+] = \mathbf{3.98\times10^{-8}\ mol\ L^{-1}}$.

$$[OH^-] = \frac{1\times10^{-14}}{3.98\times10^{-8}} = \mathbf{2.5\times10^{-7}\ mol\ L^{-1}}$$

62. $2.32 = -\log[H_3O^+]$

$\log[H_3O^+] = -2.32$

or $[H_3O^+] = \mathbf{4.8\times10^{-3}\ mol\ L^{-1}}$

$$[OH^-] = \frac{1\times10^{-14}}{4.8\times10^{-3}} = \mathbf{2.08\times10^{-12}\ mol\ L^{-1}}.$$

63. $-\log[H^+] = 3.76$

$[H^+] = \mathbf{1.73\times10^{-4}\ M}$

64. *(i)* $-\log[H_3O^+] = 7.38$

$\therefore\ [H_3O^+] = \mathbf{4.17\times10^{-8}\ M}$

(ii) $-\log[H_3O^+] = 6.4$

$[H_3O^+] = \mathbf{3.98\times10^{-7}\ M}$

(iii) $-\log[H_3O^+] = 1.2$

$[H_3O^+] = \mathbf{6.3\times10^{-2}\ M}$

(iv) $-\log[H_3O^+] = 6.83$

$[H_3O^+] = \mathbf{1.48\times10^{-7}\ M}$

65. $-\log[H^+] = \mathbf{1.7}$

$[H^+] = \mathbf{2.0\times10^{-2}\ mol\ L^{-1}}$

66. Concentration of $HNO_3 = \frac{0.063}{63}$

$= 0.001 = 1\times10^{-3}\ \mathbf{mol\ L^{-1}}$

Since HNO_3 is a strong electrolyte, it completely ionises as

$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$

$[H_3O^+] = \mathbf{1\times10^{-3}\ mol\ L^{-1}}$

Now, $[H_3O^+][OH^-] = 1\times10^{-14}$

or $[OH^-] = \frac{1\times10^{-14}}{1\times10^{-3}} = \mathbf{1\times10^{-11}\ mol\ L^{-1}}$.

67. *(i)* $NaOH \rightleftharpoons Na^+ + OH^-$

Since NaOH is a strong base.

$[OH^-] = [NaOH] = 0.01 = 1\times10^{-2}\ M$

Now $[H_3O^+][OH^-] = 1\times10^{-14}$

$$[H_3O^+] = \frac{1\times10^{-14}}{1\times10^{-2}} = \mathbf{1\times10^{-12}}$$

(ii) $HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$

$[H_3O^+] = [HNO_3] = \mathbf{0.1}$

Now, $[H_3O^+][OH^-] = 1\times10^{-14}$

$$[OH^-] = \frac{1\times10^{-14}}{0.1} = \mathbf{1\times10^{-13}}$$

68. $Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^-$

Since $Ba(OH)_2$ ionises completely

$\therefore\ [OH^-] = 2[Ba(OH)_2] = 2\times0.001 = 0.002\ M$

$[H_3O^+][OH^-] = 1\times10^{-14}$

$$\therefore\ [H_3O^+] = \frac{1\times10^{-14}}{[OH^-]} = \frac{1\times10^{-14}}{0.002} = \mathbf{5.0\times10^{-12}}.$$

69. $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

$$K_a = \frac{c\alpha^2}{1-\alpha} \approx c\alpha^2 \quad (\alpha \text{ is small in comparison to } 1)$$

$$\alpha = \sqrt{\frac{K_a}{c}} \text{ and } [H^+] = \sqrt{K_a.c}$$

$$\therefore\ [H^+] = \sqrt{1.8\times10^{-5}\times0.2} = \mathbf{1.897\times10^{-3}\ M}.$$

70. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

If α is the degree of dissociation, then

$[H^+] = c.\alpha$

$\therefore\ [H^+] = 0.1\times0.0132 = \mathbf{1.32\times10^{-3}\ M}.$

71. Moles of NaOH $= \frac{2.0}{40}$

Moles per litre of solution

= Molarity = 0.05 M

$NaOH \rightleftharpoons Na^+ + OH^-$

$[OH^-] = [NaOH] = 0.05\ M = 5\times10^{-2}$

$$[H_3O^+] = \frac{1\times10^{-14}}{5\times10^{-2}} = 2.0\times10^{-13}$$

$pH = -\log[H_3O^+] = -\log(2.0\times10^{-13}) = \mathbf{12.7}.$

72. Moles of $HNO_3 = \frac{0.63}{63} = 0.01\ M$

$$\text{Molarity} = \frac{0.01}{10}\times1 = 0.001 = 1\times10^{-3}$$

$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$

$[H_3O^+] = [HNO_3] = 1\times10^{-3}$

$pH = -\log(1\times10^{-3}) = \mathbf{3}$

73. $$[TlOH] = \frac{\frac{2}{221}}{2} = 0.0045\ \text{mol L}^{-1}$$

$TlOH \rightleftharpoons Tl^+ + OH^-$

$[OH^-] = 0.0045\ M$

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$$\therefore \quad [H^+] = \frac{1\times10^{-14}}{0.0045} = 2.22\times10^{-12}\ M$$

$$pH = -\log[H^+]$$
$$= -\log(2.22\times10^{-12}) = \mathbf{11.65.}$$

74. Degree of ionisation $= \frac{2.3}{100} = \mathbf{0.023}$

Now, $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

Initial conc.	c	0	0
Equi. conc.	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$\therefore \quad [H_3O^+] = C\alpha = 0.002\times0.023 = 4.6\times10^{-5}$

$pH = -\log[H_3O^+] = -\log(4.6\times10^{-5})$
$= -(0.66-5) = \mathbf{4.34.}$

75. $CH_3COOH\,(aq) + H_2O \rightleftharpoons H_3O^+\,(aq) + CH_3COO^-\,(aq)$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H_3O^+]^2}{[CH_3COOH]}$$

$$1.8\times10^{-5} = \frac{[H_3O^+]^2}{0.15}$$

or $[H_3O^+] = \sqrt{1.8\times10^{-5}\times0.15}$
$= 1.64\times10^{-3}\ mol\ L^{-1}$

$pH = -\log[H_3O^+] = -\log(1.64\times10^{-3})$
$= -(0.21-3) = \mathbf{2.79.}$

76. Concentration of NaOH

$$[NaOH] = \frac{0.3}{40}\times\frac{1000}{200} = 0.0375\ M$$

$\therefore \quad [OH^-] = 0.0375\ M$

$$[H_3O^+] = \frac{1\times10^{-14}}{0.0375} = 2.67\times10^{-13}\ M$$

$pH = -\log[H_3O^+]$
$= -\log(2.67\times10^{-13}) = \mathbf{12.57.}$

77. $pH = -\log[H_3O^+]$

$[H_3O^+] = 1\times10^{-4}\ M$

Concentration of solution $= \frac{0.0250}{250}\times1000 = 0.1M$

Initial conc.	HA	+ H_2O ⇌	H_3O^+	+ A^-
	0.1 M		0	0
At equi.	$0.1-1\times10^{-4}$		1×10^{-4}	1×10^{-4}

$$K_a = \frac{(1\times10^{-4})\times(1\times10^{-4})}{0.1-1\times10^{-4}}$$

or $= \frac{(1\times10^{-4})\times(1\times10^{-4})}{0.1} = \mathbf{1\times10^{-7}}$

78. $[HCl] = \frac{0.1\times25}{500}$
$= 0.005 = 5\times10^{-3}\ M$

$pH = -\log[H_3O^+]$
$= -\log(5\times10^{-3}) = -(0.698-3)$
$= \mathbf{2.302.}$

79. $pH = -\log[H_3O^+]$

$[H_3O^+] = 2.51\times10^{-11}$

Now, $[H_3O^+][OH^-] = 1\times10^{-14}$

$$[OH^-] = \frac{1\times10^{-14}}{[H_3O^+]} = \frac{1\times10^{-14}}{2.51\times10^{-11}} = 3.98\times10^{-4}$$

$NaOH \longrightarrow Na^+ + OH^-$

$[OH^-] = [NaOH] = 3.98\times10^{-4}$

Wt. of NaOH dissolved per litre
$= 3.98\times10^{-4}\times40 = \mathbf{1.59\times10^{-2}\ g.}$

80. Diethyl hydroxide ion ionizes in aqueous solution as:

$(C_2H_5)_2NH + H_2O \longrightarrow (C_2H_5)_2NH_2OH$

$(C_2H_5)_2NH_2OH \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$

Initial conc.	c	0	0
At equi.	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$$K_b = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \quad \text{or} \approx c\alpha^2$$

$[OH^-] = c\alpha$

Now, $-\log[H_3O^+] = 12$

$[H_3O^+] = 10^{-12}$

$$\therefore \quad [OH^-] = \frac{1\times10^{-14}}{1\times10^{-12}} = 10^{-2}$$

$$\therefore \quad 10^{-2} = 0.05\alpha \quad \text{or} \quad \alpha = \frac{10^{-2}}{0.05} = 0.2$$

Now, $K_b = c\alpha^2 = 0.05\times(0.2)^2$
$= \mathbf{2\times10^{-3}.}$

81. $pH = 3.44$

$[H^+] = 3.63\times10^{-4}\ M$

Now, $[H^+] = \sqrt{K_a.c}$

$3.63\times10^{-4} = \sqrt{K_a(0.02)}$

$$K_a = \frac{(3.63\times10^{-4})^2}{0.02} = 6.59\times10^{-6}$$

K_a (acid) $\times$ K_b (conjugate base) $= 10^{-14}$

K_a (pyridinium hydrochloride) $\times$ K_b (pyridine)
$= 10^{-14}$

$$\therefore \quad K_b \text{ (pyridine)} = \frac{10^{-14}}{6.59\times10^{-6}}$$
$$= \mathbf{1.51\times10^{-9}.}$$

82. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Degree of dissociation of acetic acid,

$$\alpha = \sqrt{\frac{K_a}{c}}$$

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$$= \sqrt{\frac{1.74\times10^{-5}}{0.05}}$$

$$= \mathbf{1.86 \times 10^{-2}\ or\ 1.86\%.}$$

$$[CH_3COO^-] = c\alpha = 0.05 \times 1.86 \times 10^{-2}$$

$$= 9.3 \times 10^{-4}$$

$$[H_3O^+] = [CH_3COO^-] = 9.3 \times 10^{-4}$$

$$pH = -\log [H_3O^+] = -\log (9.3 \times 10^{-4})$$

$$= \mathbf{3.03}$$

83. Moles of $Ba(OH)_2$ in 50 ml of 0.01 M $Ba(OH)_2$

$$= \frac{0.01}{1000} \times 50 = 5 \times 10^{-4}$$

Since volume is made to 100 mL, the concentration of $Ba(OH)_2$ in dilute solution,

$$c = \frac{5\times10^{-4}}{100} \times 1000 = 5 \times 10^{-3}\ M$$

$$Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^-$$

$$\therefore\ [OH^-] = 2 \times [Ba(OH)_2] = 2 \times 5 \times 10^{-3} = 10^{-2}\ M$$

$$[H_3O^+] = \frac{1\times10^{-14}}{[OH^-]} = \frac{1\times10^{-14}}{10^{-2}} = 10^{-12}\ M$$

$$pH = -\log [H_3O^+] = -\log (10^{-12}) = \mathbf{12.}$$

84.

$$C_6H_5NH_2 \overset{H_2O}{\rightleftharpoons} C_6H_5NH_3^+ + OH^-$$

Initial conc.	c	0	0
Equi. conc	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$$K_b = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} \approx c\alpha^2$$

$$4.3 \times 10^{-10} = 0.01 \times \alpha^2$$

or $$\alpha = \sqrt{\frac{4.3\times10^{-10}}{0.01}} = 2.07 \times 10^{-4}$$

$$[OH^-] = c\alpha = 0.01 \times 2.7 \times 10^{-4} = 2.7 \times 10^{-6}$$

$$[H_3O^+] = \frac{1\times10^{-14}}{2.07\times10^{-6}} = 4.83 \times 10^{-9}$$

$$pH = -\log [H_3O^+] = -\log (4.83 \times 10^{-9})$$

$$= \mathbf{8.32.}$$

85.

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$$

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{[H_3O^+]^2}{[HNO_2]}$$

Now, $pH = 2$

$$-\log [H_3O^+] = 2$$

$$\therefore\ [H_3O^+] = 10^{-2}$$

$$4.5 \times 10^{-4} = \frac{(10^{-2})^2}{[HNO_2]}$$

$$[HNO_2] = \frac{10^{-4}}{4.5\times10^{-4}} = \mathbf{0.222\ M.}$$

86.

$$pH = 9.95$$

$$[H_3O^+] = 1.12 \times 10^{-10}$$

$$[OH^-] = \frac{1\times10^{-14}}{1.12\times10^{-10}} = 8.92 \times 10^{-5}$$

Now, $[OH^-] = \sqrt{K_b.c}$

$$8.92 \times 10^{-5} = \sqrt{K_b(0.005)}$$

or $$K_b = \frac{(8.92\times10^{-5})^2}{0.005} = \mathbf{1.591 \times 10^{-6}}$$

$$pK_b = -\log K_b = -\log (1.591 \times 10^{-6})$$

$$= \mathbf{5.8}$$

87. Moles of KOH $= \frac{0.561}{56}$

Molarity of solution $= \frac{0.561\times1000}{56\times200}$

$= 0.05$ M

Since KOH ionizes completely.

$$KOH = K^+ + OH^-$$

$$[K^+] = 0.05\ M, [OH^-] = 0.05\ M$$

$$[H^+] = \frac{1\times10^{-14}}{0.05} = \mathbf{2.0 \times 10^{-13}\ M.}$$

$$pH = -\log [2.0 \times 10^{-13}]$$

$$= -(0.3010 - 13) = \mathbf{12.70}$$

88. Degree of ionisation of dimethylamine,

$$\alpha = \sqrt{\frac{K_b}{c}}$$

$$K_b = 5.4 \times 10^{-4}, \qquad c = 0.02\ M$$

$$\therefore\ \alpha = \sqrt{\frac{5.4\times10^{-4}}{0.02}} = 0.1643$$

When the solution contains 0.01 M NaOH also, then

Concentration of OH^- from base $= x$

Conc. of OH^- ion from NaOH $= 0.1$

Total OH^- conc. $= 0.1 + x$

Putting these values in dissociation constant,

$$K_b = 5.4 \times 10^{-4} = \frac{x(0.1+x)}{c-x} \approx \frac{0.1x}{c}$$

$$x = \frac{5.4\times10^{-4}\times0.02}{0.1} = 1.08\times10^{-4}$$

Degree of dissociation $= \frac{1.08\times10^{-4}}{0.02} = \mathbf{0.0054.}$

89. K_a (propanoic acid) $= 1.32 \times 10^{-5}$

If α is the degree of dissociation,

$$\alpha = \sqrt{\frac{K_a}{c}}$$

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$$\alpha = \sqrt{\frac{1.32\times10^{-5}}{0.05}} = \mathbf{1.62 \times 10^{-2}}$$

$[H^+] = c\alpha = 0.05 \times 1.62 \times 10^{-2} = 8.12 \times 10^{-4}$

$pH = -\log [H^+]$

$= -\log (8.12 \times 10^{-4}) = \mathbf{3.09.}$

In the presence of 0.01 M HCl,

$\alpha = \mathbf{1.32 \times 10^{-3}.}$

90. (*i*) $H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^-$

$H_2PO_3^- \rightleftharpoons H^+ + HPO_3^{2-}$

The H^+ comes mainly from first stage

$$K_{a_1} = \frac{[H^+][H_2PO_3]}{[H_3PO_3]}$$

Let $[H^+] = x$, then $[H_2PO_3^-] = x$ and

$[H_3PO_3] = 0.01 - x \approx 0.01$

$$5 \times 10^{-2} = \frac{x \times x}{0.01}$$

$$x = \sqrt{5\times10^{-2}\times0.01} = 2.236 \times 10^{-2}$$

$pH = -\log [H^+]$

$= -\log (2.236 \times 10^{-2}) = \mathbf{1.651.}$

91. Most of the H^+ ions result from first ionization :

$H_2S \rightleftharpoons H^+ + HS^-$

$$K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]}$$

Let $[H^+] = x$, $[HS^-] = x$, $[H_2S] = 0.02 - x \approx 0.02$

$$1.3 \times 10^{-7} = \frac{x \times x}{0.02}$$

$x^2 = 1.3 \times 10^{-7} \times 0.02$

or $x = 5.10 \times 10^{-5}$

$pH = -\log [H^+] = -\log (5.10 \times 10^{-5})$

$= \mathbf{4.29.}$

92. The second dissociation constant is very very small than first dissociation constant and therefore, the concentration of H_3O^+ is obtained only from the first dissociation :

	$H_2S + H_2O \rightleftharpoons$	$H_3O^+ +$	HS^-
Initial conc.	0.10	0	0
At equilibrium	$0.10 - x$	x	x

(x is amount of H_2S dissociated)

$$K_{a_1} = \frac{[H_3O^+][HS^-]}{[H_2S]} = 9.1 \times 10^{-8}$$

or $$\frac{x\times x}{(0.10-x)} = 9.1 \times 10^{-8}$$

Solving $x = 9.5 \times 10^{-5}$

$\therefore$ $[H_3O^+] = [HS^-] = 9.5 \times 10^{-5}$ mol L^{-1}

$pH = -\log [H_3O^+] = -\log (9.5 \times 10^{-5})$

$= -\log 9.5 + 5 = -0.98 + 5 = \mathbf{4.02}$

$[H_2S] = 0.10 - 9.5 \times 10^{-5} = 0.10$ M

To calculate the concentration of S^{2-} ion, we are to consider the second dissociation :

	$HS^- + H_2O \rightleftharpoons$	$H_3O^+ +$	S^{2-}
Initial conc.	9.5×10^{-5}	9.5×10^{-5}	0
At equi.	$9.5 \times 10^{-5} - x$	$9.5 \times 10^{-5} + x$	x

$$K_{a_2} = \frac{[H_3O^+][S^{2-}]}{[HS^-]}$$

$$= \frac{(9.5\times10^{-5} + x)\times x}{(9.5\times10^{-5} - x)}$$

Assuming x to be very very small :

$9.5 \times 10^{-5} - x \approx 9.5 \times 10^{-5}$ and $9.5 \times 10^{-5} + x$

$= 9.5 \times 10^{-5}$

Solving $x = 1.3 \times 10^{-13}$

$\therefore$ $[S^{2-}] = 1.3 \times 10^{-13}$

Thus, $[H_3O^+] = 9.5 \times 10^{-5}$ M,

$[HS^-] = 9.5 \times 10^{-5}$ M,

$[S^{2-}] = 1.3 \times 10^{-13}$ M, $[H_2S] = 0.01$ M, pH = 4.02.

93. $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

$$K_h = \frac{K_w}{K_b}$$

$K_b = 1.81 \times 10^{-5}$, $K_w = 1.0 \times 10^{-14}$

$$K_h = \frac{1.0\times10^{-14}}{1.81\times10^{-5}} = 5.52 \times 10^{-10}$$

$$h = \sqrt{\frac{K_w}{K_b.c}} = \sqrt{\frac{1.0\times10^{-14}}{1.81\times10^{-5}\times0.01}}$$

$= 2.35 \times 10^{-4}$

$[H^+] = ch = 0.01 \times 2.35 \times 10^{-4}$

$= \mathbf{2.35 \times 10^{-6}}$

$pH = -\log [H^+] = -\log (2.35 \times 10^{-6})$

$= \mathbf{5.63.}$

94. $$h = \sqrt{\frac{K_w}{K_a.K_b}}$$

$K_a = 1.75 \times 10^{-5}$, $K_b = 1.81 \times 10^{-5}$

$$h = \sqrt{\frac{1.0\times10^{-14}}{1.75\times10^{-5}\times1.81\times10^{-5}}}$$

$= \mathbf{5.62 \times 10^{-3}.}$

95. $$h = \sqrt{\frac{K_w}{K_a.c}}$$

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$K_w = 1.0 \times 10^{-14}$, $K_a = 1.8 \times 10^{-5}$, $c = 0.1$

$$h = \sqrt{\frac{1.0\times10^{-14}}{1.8\times10^{-5}\times0.1}}$$

$$= 7.45 \times 10^{-5} \text{ 0r } 0.00745\%$$

96. $$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

$pK_a = pK_b$

$$pH = \frac{1}{2} \times 14 = \mathbf{7.}$$

97. $$h = \sqrt{\frac{K_w}{K_a.c}} = \sqrt{\frac{1.0\times10^{-14}}{4.8\times10^{-10}\times0.25}}$$

$$= 9.13 \times 10^{-3}$$

$K_a = 4.8 \times 10^{-10}$

$pK_a = -\log(4.8 \times 10^{-10}) = 9.32$

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log c$$

$$= \frac{1}{2}(14) + \frac{1}{2}(9.32) + \frac{1}{2}\log(0.25)$$

$$= 7 + 4.66 - 0.30$$

$$= \mathbf{11.36.}$$

98. $pK_a = -\log K_a = 4.76$ $\quad K_a = 1.74 \times 10^{-5}$

$pK_b = -\log K_b = 4.75$ $K_b = 1.77 \times 10^{-5}$

$$K_h = \frac{K_w}{K_a.K_b}$$

$$= \frac{1.0\times10^{-14}}{1.74\times10^{-5}\times1.77\times10^{-5}} = \mathbf{3.25 \times 10^{-5}}$$

$$h = \sqrt{\frac{K_w}{K_a.K_b}}$$

$$= \sqrt{3.25\times10^{-5}} = \mathbf{5.7 \times 10^{-3}}$$

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

$$= \frac{1}{2}\times14 + \frac{1}{2}\times4.76 - \frac{1}{2}\times4.75$$

$$= \mathbf{7.005.}$$

The value is same for both concentrations.

99. $$h = \sqrt{\frac{K_w}{K_a.K_b}}$$

$$= \sqrt{\frac{1.0\times10^{-14}}{(1.77\times10^{-5})\times(4.99\times10^{-10})}}$$

$$= \mathbf{1.06}$$

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

$pK_a = -\log(1.77 \times 10^{-5})$

$= -(0.25 - 5) = 4.75$

$pK_b = -\log(4.98 \times 10^{-10})$

$= -(0.70 - 10) = 9.30$

$$pH = \frac{1}{2}(14) + \frac{1}{2}(4.75) - \frac{1}{2}(9.30)$$

$$= \mathbf{4.725}$$

100. $$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \log c$$

$pK_a = -\log K_a = -\log(4.5 \times 10^{-4})$

$= -(0.65 - 4) = 3.35$

$$\therefore \quad pH = \frac{1}{2}(14) + \frac{1}{2}(3.35) + \log 0.04$$

$$= 7 + 1.675 - 1.39 = \mathbf{7.285}$$

$$h = \sqrt{\frac{K_w}{K_a.c}}$$

$$= \sqrt{\frac{1\times10^{-14}}{4.5\times10^{-4}\times0.04}} = \mathbf{2.35 \times 10^{-5}}$$

101. $$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$$7.40 = 6.37 + \log\frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\log\frac{[HCO_3^-]}{[H_2CO_3]} = 1.03$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \mathbf{10.7.}$$

102. $pH = pK_a + \log\frac{[Salt]}{[Acid]}$

$pK_a = 4.74$, [Salt] = 0.04 M, [Acid] = 0.08 M

$$pH = 4.74 + \log\frac{(0.04)}{(0.08)}$$

$pH = 4.74 + (-0.30) = \mathbf{4.44}$.

103. For HClO, $K_a = 3.0 \times 10^{-8}$

$pK_a = -\log K_a$

$= -\log(3.0 \times 10^{-8}) = 7.523$

Now, $$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$$6.50 = 7.523 + \log\frac{[ClO^-]}{[HClO]}$$

$$\log\frac{[ClO^-]}{[HClO]} = 6.50 - 7.523 = -1.023$$

$$\therefore \quad \frac{[ClO^-]}{[HClO]} = 9.48 \times 10^{-2}$$

$\therefore$ Ratio is $9.48 \times 10^{-2} : 1$

104. Solubility of CaF_2

$$= \frac{1.7\times10^{-3}}{100} \times 1000 = 1.7 \times 10^{-2} \text{ g } L^{-1}$$

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Mol. wt. of $CaF_2 = 40 + 2 \times 19 = 78$

$\therefore$ Solubility $= \frac{1.7 \times 10^{-2}}{78}$

$= 2.18 \times 10^{-4}$ mol L^{-1}

$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$

$[Ca^{2+}] = 2.18 \times 10^{-4}$ mol L^{-1},

$[F^-] = 2 \times 2.18 \times 10^{-4}$

$= 4.36 \times 10^{-4}$ mol L^{-1}

$K_{sp} = [Ca^{2+}][F^-]^2$

$= (2.18 \times 10^{-4})(4.36 \times 10^{-4})^2$

$=$ **4.14×10^{-11}.**

105. $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

Solubility of $Ag_2CrO_4 = 8.0 \times 10^{-5}$ mol L^{-1}

$[Ag^+] = 2 \times 8.0 \times 10^{-5}$

$= 1.6 \times 10^{-4}$ mol L^{-1},

$[CrO_4^{2-}] = 8.0 \times 10^{-5}$ mol L^{-1}

$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

$= (1.6 \times 10^{-4})^2 \times (8.0 \times 10^{-5})$

$=$ **2.048×10^{-12}.**

106. $Al_2(SO_4)_3 \rightleftharpoons 2Al^{3+} + 3SO_4^{2-}$

If solubility of $Al_2(SO_4)_3 = x$, then

$[Al^{3+}] = 2x$, $[SO_4^{2-}] = 3x$

$K_{sp} = [Al^{3+}]^2[SO_4^{2-}]^3$

$= (2x)^2 \times (3x)^3 =$ **$108\,x^5$**

107. $AgCl \rightleftharpoons Ag^+ + Cl^-$

Solubility of AgCl = 0 .00198 g L^{-1}

$= \frac{0.00198}{143.5} = 1.38 \times 10^{-5}$ mol L^{-1}

$[Ag^+] = 1.38 \times 10^{-5}$ mol L^{-1},

$[Cl^-] = 1.38 \times 10^{-5}$ mol L^{-1}

$K_{sp} = [Ag^+][Cl^-] = (1.38 \times 10^{-5})(1.38 \times 10^{-5})$

$=$ **1.90×10^{-10}.**

108. Concentration of $Mg(OH)_2 = \frac{8.35 \times 10^{-3}}{58}$

$= 1.44 \times 10^{-4}$ mol L^{-1}

$Mg(OH)_2 = Mg^{2+} + 2OH^-$

$[Mg^{2+}] = 1.44 \times 10^{-4}$ M,

$[OH^-] = 2.88 \times 10^{-4}$ M

$K_{sp} = [Mg^{2+}][OH^-]^2$

$K_{sp} = (1.44 \times 10^{-4}) \times (2.88 \times 10^{-4})^2$

$=$ **1.194×10^{-11}.**

109. (*i*) **Silver chromate, Ag_2CrO_4**

$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$[Ag^+] = 2s$, $CrO_4^{2-} = s$

$K_{sp} = (2s)^2(s) = 4s^3$

$\therefore \quad 4s^3 = 1.1 \times 10^{-12}$

$s = \left(\frac{1.1 \times 10^{-12}}{4}\right)^{1/3} = 6.5 \times 10^{-5}$

$[Ag^+] = 1.30 \times 10^{-4}$ M,

$[CrO_4^{2-}] =$ **6.5×10^{-5} M**

(*ii*) **Barium chromate, $BaCrO_4$**

$BaCrO_4 \rightleftharpoons Ba^{2+} + CrO_4^{2-}$

$[Ba^{2+}] = s$, $CrO_4^{2-} = s$

$K_{sp} = (s)(s) = s^2$

$s^2 = 1.2 \times 10^{-10}$

$s = (1.2 \times 10^{-10})^{1/2} = 1.09 \times 10^{-5}$M

$[Ba^{2+}] = 1.09 \times 10^{-5}$ M,

$[CrO_4^{2-}] =$ **1.09×10^{-5} M**

(*iii*) **Ferric hydroxide, $Fe(OH)_3$**

$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$

$[Fe^{3+}] = s$, $[OH^-] = 3s$

$K_{sp} = (s)(3s)^3 = 27s^4$

$27s^4 = 1.0 \times 10^{-38}$

$s = \left(\frac{1.0 \times 10^{-38}}{27}\right)^{1/4}$

$= 1.38 \times 10^{-10}$ M

$[Fe^{3+}] = 1.38 \times 10^{-10}$ M,

$[OH^-] =$ **4.14×10^{-10} M**

(*iv*) **Lead chloride, $PbCl_2$**

$PbCl_2 \rightleftharpoons Pb^{2+} + 2\,Cl^-$

$[Pb^{2+}] = s$, $[Cl^-] = 2s$

$K_{sp} = (s) \times (2s)^2 = 4\,s^3$

$4\,s^3 = 1.6 \times 10^{-5}$

$s = \left(\frac{1.6 \times 10^{-5}}{4}\right)^{1/3} = 1.59 \times 10^{-2}$ M

$[Pb^{2+}] = 1.59 \times 10^{-2}$ M,

$[Cl^-] =$ **3.18×10^{-2} M**

(*v*) **Mercurous iodide, Hg_2I_2**

$Hg_2I_2 \rightleftharpoons 2\,Hg^+ + 2\,I^-$

$[Hg^+] = 2s$, $[I^-] = 2s$

$K_{sp} = (2s)^2(2s)^2$

$= 16s^4$

$16s^4 = 4.5 \times 10^{-29}$

$s = \left(\frac{4.5 \times 10^{-29}}{16}\right)^{1/4} = 4.09 \times 10^{-8}$ M

$[Hg^+] = 8.18 \times 10^{-8}$ M,

$[I^-] =$ **8.18×10^{-8} M.**

110. $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

Let the solubility of $Mg(OH)_2$ is x.

$[Mg^{2+}] = x$, $[OH^-] = 2x$

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$$K_{sp} = [Mg^{2+}][OH^-]^2$$
$$= (x) \times (2x)^2 = 5 \times 10^{-12}$$
or $$4x^3 = 5 \times 10^{-12} \text{ or } x^3 = 1.25 \times 10^{-12}$$
or $$x = (1.25 \times 10^{-12})^{1/3}$$
$$= \mathbf{1.08 \times 10^{-4} \text{ mol } L^{-1}}.$$

111. $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

Let the solubility of Ag_2CrO_4 is x.

$$\therefore [Ag^+] = 2x, [CrO_4^{2-}] = x$$
$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$
$$= (2x)^2 \times x = 1.9 \times 10^{-12}$$
$$4x^3 = 1.9 \times 10^{-12} \text{ or}$$
$$x = \left(\frac{1.9}{4} \times 10^{-12}\right)^{1/3}$$
$$= \mathbf{7.8 \times 10^{-5} \text{ mol } L^{-1}}$$

112. $Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$

Let the solubility of $Fe(OH)_3$ is x.

$$[Fe^{3+}] = x, [OH^-] = 3x$$
$$K_{sp} = [Fe^{3+}][OH^-]^3$$
$$= x \times (3x)^3 = 27x^4$$
$$\therefore 27x^4 = 1.1 \times 10^{-36}$$
or $$x = \left(\frac{1.1 \times 10^{-36}}{27}\right)^{1/4}$$
$$= 0.449 \times 10^{-9} \text{ mol } L^{-1}$$
$$= \mathbf{4.8 \times 10^{-8} \text{ g } L^{-1}}.$$

113. $CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$

Let its solubility is s,

$$[Ca^{2+}] = s, [F^-] = 2s$$
$$K_{sp} = [Ca^{2+}][F^-]^2$$
$$= (s)(2s) = 4s^3$$
$$\therefore 4s^3 = 1.7 \times 10^{-10}$$
$$s = \left(\frac{1.7 \times 10^{-10}}{4}\right)^{1/3}$$
$$= \mathbf{3.49 \times 10^{-4} \text{ M}}.$$

114. $BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$

$$K_{sp} = [Ba^{2+}][F^-]^2$$

On mixing 100 mL of $Ba(NO_3)_2$ and 200 mL of KF, the solution becomes 300 mL.

$$\text{Conc. of } Ba(NO_3)_2 = \frac{1.0 \times 10^{-3} \times 100}{300}$$
$$= 3.33 \times 10^{-2} \text{ M}$$

$$\text{Conc. of KF} = \frac{1.0 \times 10^{-3} \times 200}{3} = 6.66 \times 10^{-2} \text{ M}$$

$$Ba(NO_3)_2 \rightleftharpoons Ba^{2+} + 2NO_3^-$$
$$[Ba^{2+}] = [Ba(NO_3)_2] = 3.33 \times 10^{-2} \text{ M}$$
$$[F^-] = [KF] = 6.66 \times 10^{-2} \text{ M}$$

Now, ionic product $= [Ba^{2+}][F^-]^2$
$$= (3.33 \times 10^{-2})(6.66 \times 10^{-2})^2$$
$$= \mathbf{1.47 \times 10^{-4}}$$

Since ionic product is more than K_{sp}, precipitation can occur.

115. Total volume = 50 + 150 = 200 mL

$$[Ca(NO_3)_2] \text{ after mixing} = \frac{0.04}{200} \times 50 = 0.01 \text{ M}$$

$$[(NH_4)_2SO_4] \text{ after mixing} = \frac{0.08}{200} \times 150 = 0.06$$

$$Ca(NO_3)_2 \rightleftharpoons Ca^{2+} + 2NO_3^-$$
$$\therefore [Ca^{2+}] = 0.01 \text{ M}$$
$$(NH_4)_2SO_4 \rightleftharpoons 2NH_4^+ + SO_4^{2-}$$
$$\therefore [SO_4^{2-}] = 0.06 \text{ M}$$

Ionic product, $[Ca^{2+}][SO_4^{2-}]$
$= 0.06 \times 0.01 = 6.0 \times 10^{-4}$

Since ionic product is more than K_{sp}, **precipitation will occur.**

116. Ionic product, $[Zn^{2+}][S^{2-}]$
$$= 0.1 \times 8.1 \times 10^{-31} = 8.1 \times 10^{-32}$$
$$K_{sp} \text{ (ZnS)} = 3.0 \times 10^{-23}$$
Ionic product, $[Cu^{2+}][S^{2-}]$
$$= 0.01 \times 8.1 \times 10^{-31} = 8.1 \times 10^{-33}$$
$$K_{sp} \text{ (CuS)} = 8.0 \times 10^{-34}$$

Since ionic product of CuS is greater than K_{sp}, **precipitation of CuS will occur.**

117. $[Ba^{2+}] = [BaCl_2] = 7.0 \times 10^{-8}$

Now, $[Ba^{2+}][SO_4^{2-}] = 1.4 \times 10^{-10}$

$$\text{or } [SO_4^{2-}] = \frac{1.4 \times 10^{-10}}{7.0 \times 10^{-8}} = 2 \times 10^{-3}$$
$$[SO_4^{2-}] = [H_2SO_4] = \mathbf{2 \times 10^{-3} \text{ mol } L^{-1}}.$$

118. Solubility equilibrium is

$$Al(OH)_3(s) \rightleftharpoons Al^{3+} + 3OH^-$$
$$K_{sp} = [Al^{3+}][OH^-]^3$$

Let us calculate the concentration of $AlCl_3$ and NaOH in 10^3 (diluted) solution. On mixing $\frac{1}{2}$ L of 4×10^{-2} M NaOH and $\frac{1}{2}$ L of 2×10^{-3} M $AlCl_3$ solution and on dilution the total volume is made 10^3 L.

$\frac{1}{2}$ L of 4×10^{-2} M NaOH is diluted to 10^3 L.

$$\text{Now, } [NaOH] = \frac{4 \times 10^{-2} \times 1/2}{10^3} = 2 \times 10^{-5} \text{ M}$$

$$NaOH \rightleftharpoons Na^+ + OH^-$$
$$[OH^-] = [NaOH] = 2 \times 10^{-5} \text{ M}$$

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Solution File

Similarly,

$\frac{1}{2}$ L of 2×10^{-3} M $AlCl_3$ is diluted to 10^3 L.

Now, $[AlCl_3] = \frac{2\times10^{-3}\times1/2}{10^3} = 1 \times 10^{-6}$ M

Now, $AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^-$

$[Al^{3+}] = [AlCl_3] = 1 \times 10^{-6}$ M

Ionic product of $Al(OH)_3 = [Al^{3+}][OH^-]^3$

$= (1 \times 10^{-6})(2 \times 10^{-5})^3$

$= \mathbf{8 \times 10^{-21}}$

Since ionic product is greater than solubility product (K_{sp}), precipitation will occur.

119. Conc. of $NaIO_3$ after mixing

$= \frac{0.002}{2} = 0.001$ M

Conc. of $Cu(ClO_3)_2$ after mixing

$= \frac{0.002}{2} = 0.001$ M

$NaIO_3 \rightleftharpoons Na^+ + IO_3^-$

$[IO_3^-] = 0.001$ M

$Cu(ClO_3)_2 \rightleftharpoons Cu^{2+} + 2\,ClO_3^-$

$[Cu^{2+}] = 0.001$ M

Ionic product of $Cu(IO_3)_2$

$= [Cu^{2+}][IO_3^-]^2$

$= (0.001) \times (0.001)^2$

$= \mathbf{1 \times 10^{-9}}$

Since ionic product is less than K_{sp} (7.4×10^{-4}), no precipitation will occur.

Chapter Summary

Key Terms & Laws

- **Equilibrium.** The state at which the measurable properties of the system (pressure, density, colour, concentration, etc.) do not undergo any further noticeable change under given set of conditions is said to be a state of equilibrium.
- **Law of mass action.** The rate of a chemical reaction at any particular temperature is proportional to the product of the molar concentration of reactants with each concentration term raised to the power equal to the number of molecules of the respective reactants (called stoichiometric coefficients in the balanced chemical equation.
- **Equilibrium constant.** It is the ratio between the products of molar concentrations of the products to that of the molar concentrations of the reactants, which each concentration term raised to a power equal to its stoichiometric coefficients in the balanced chemical equation at a constant temperature.
  It is also equal to ratio of rate constant of forward reaction and backward reaction.
- **Le-Chatelier's principle.** If an equilibrium is subjected to any kind of stress (change in concentration, pressure or temperature, etc.) equilibrium shifts in such a way so as to undo the effect of stress imposed.
- **Ionic equilibrium.** The equilibrium established between the unionised molecules and the ions in solution of weak electrolytes.
- **pH** is the negative logarithm of the H_3O^+ ion concentration in moles per litre.
- **Hydrolysis**. The reaction of anion or cation of the salt with water to produce an acidic or basic solution.
- **Indicators**. The substances which indicate by change in colour, the completion of a chemical reaction.
- **Solubility product**. The product of the concentrations of its ions in the saturated solution with each concentration term raised to the power equal to the number of ions produced on dissociation of one mole of the substance.
- **Common ion effect.** The supression of the degree of dissociation of a weak acid or a weak base by the addition of a strong electrolyte containing a common ion.
- **Buffer solution.** The solution which resists changes in the hydrogen ion concentration (*p*H value) on the addition of small amount of acid or base.

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QUICK CHAPTER ROUND UP

EQUILIBRIUM
State at which measurable properties do not change with time

Homogeneous
- Reactants and products in same phase

Heterogeneous
- Reactants and products in different phases

At equilibrium
- Rate of forward reaction = Rate of backward reaction
- $\Delta G = 0$ so that $\Delta H = T\Delta S$
- dynamic in nature

Characteristics of Equilibrium
- can be attained if the system is closed
- can be approached from either direction
- a catalyst does not alter the equilibrium point

$$aA + bB = cC + dD$$

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

$$K_p = \frac{(p_C)^c\,(p_D)^d}{(p_A)^a\,(p_B)^b}$$

$$K_p = K_c\,(RT)^{\Delta n_g}$$

Δn_g = No. of moles of products − No. of moles of reactants

The relation between equilibrium constants for a general reaction and its multiples :

$aA + bB \rightleftharpoons cC + dD$	K
$cC + dD \rightleftharpoons aA + bB$	$K_1 = \frac{1}{K}$
$naA + nbB \rightleftharpoons ncC + ndD$	$K_2 = K^n$
$\frac{1}{n}aA + \frac{1}{n}bB \rightleftharpoons \frac{1}{n}cC + \frac{1}{n}dD$	$K_3 = K^{1/n}$

Le-Chatelier's Principle

1. **Effect of concentration**
   - addition of reactants shifts equilibrium in forward direction.
   - addition of products shifts equilibrium in backward direction.
2. **Effect of temperature**
   - increase of temperature shifts equilibrium in endothermic direction.
   - decrease of temperature shifts equilibrium in exothermic direction.
3. **Effect of pressure**
   - increase of pressure shifts equilibrium in the direction of lesser number of moles.
   - decrease of pressure shifts equilibrium in the direction of larger number of moles.
4. **Effect of catalyst**
   - a catalyst does not affect equilibrium constant.

IONIC EQUILIBRIUM
Equilibrium established between unionised molecules and ions in solution

$$AB \rightleftharpoons A^+ + B^-$$

$$K = \frac{[A^+]\,[B^-]}{[AB]}$$

$\Rightarrow$ If α is the degree of dissociation

$$K = \frac{c\alpha^2}{1-\alpha} \quad \text{or} \quad \alpha = \sqrt{\frac{K}{C}} \quad 1 - \alpha \approx 1$$

ACID BASE CONCEPTS

Arrhenius
- acids give H^+ ions in water
- bases give OH^- ions in water

Bronsted-Lowry
- acids donate H^+
- bases accept H^+

Lewis
- acids accept a pair of electrons
- bases donate a pair of electrons

acids = Conjugate base + H^+
base + H^+ = Conjugate acid

- Arrhenius acids are also Bronsted acids but Arrhenius bases are not Bronsted bases.
- All Bronsted bases are also Lewis bases but all Bronsted acids are not Lewis acids.

- Strong acid has weak conjugate base
- Weak acid has strong conjugate base
- Strong base has weak conjugate acid
- Weak base has strong conjugate acid

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Ionic product of water

$K_w = [H_3O^+]\,[OH^-]$
$= 1.008 \times 10^{-14}$ at 298 K

$\Rightarrow$

In acidic solution : $[H_3O^+] > [OH^-]$
In basic solution : $[H_3O^+] < [OH^-]$
In neutral solution : $[H_3O^+] = [OH^-]$

$pH = -\log [H_3O^+]$ $\quad$ $pOH = -\log [OH^-]$ $\quad$ $pH + pOH = pK_w = 14$

For neutral solution, pH = 7; Acidic solution, pH < 7; Basic solution, pH > 7

Dissociation constants of acids

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$

$$K_a = \frac{c\alpha^2}{1-\alpha} \approx c\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{c}}$$

$$[H_3O^+] = \sqrt{K_a \cdot c}$$

Dissociation constants of Bases

$BOH \rightleftharpoons B^+ + OH^-$

$$K_b = \frac{c\alpha^2}{1-\alpha} \approx c\alpha^2$$

$$\alpha = \sqrt{\frac{K_b}{c}}$$

$$[OH^-] = \sqrt{K_b \cdot c}$$

- Larger the value of pK_a weaker the acid is
- Larger the value of pK_b weaker the base is

$pK_a = -\log K_a$; $pK_b = -\log K_b$

HYDROLYSIS

For salt of weak acid and strong base

$$K_h = \frac{K_w}{K_a}$$

$$h = \sqrt{\frac{K_w}{K_a \cdot c}}$$

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log c$$

- are basic

➢ CH_3COONa, NO_2CO_3, K_2CO_3

For salt of strong acid and weak base

$$K_h = \frac{K_w}{K_b}$$

$$h = \sqrt{\frac{K_w}{K_b \cdot c}}$$

$$pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log c$$

- are acidic

➢ NH_4Cl, $CuSO_4$, $AlCl_3$

For salt of weak acid and weak base

$$K_h = \frac{K_w}{K_a \cdot K_b}$$

$$h = \sqrt{\frac{K_w}{K_a \cdot K_b}}$$

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

- are neutral or may be acidic or basic depending upon the strength of acid or base.

➢ CH_3COONH_4, $(NH_4)_2CO_3$

Salts of strong acids and strong bases do not undergo hydrolysis

Henderson's equation for buffer solution

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$ (For acidic buffer)

$$pH = 14 - pK_b - \log \frac{[Salt]}{[Base]}$$ (For basic buffer)

Solubility products for sparingly soluble salts

$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$
$K_{sp} = [A^{y+}]^x\,[B^{x-}]^y$

e.g., $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$
$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$

$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$
$K_{sp} = [Mg^{2+}]\,[OH^-]^2$

$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$
$K_{sp} = [Ag^+]^2\,[CrO_4^{2-}]$

Ionic product is greater than K_{sp} $\Rightarrow$ precipitation occurs
Ionic product is less than K_{sp} $\Rightarrow$ no precipitation occurs

Solubility from K_{sp}

- For AgCl type : $s = \sqrt{K_{sp}}$
- For $Mg(OH)_2$ type : $s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
- For $Ca_3(PO_4)_2$ type : $s = \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$

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NCERT FILE Solved

NCERT Textbook Exercises

Q.1. A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.
(a) What is the initial effect of the change on vapour pressure?
(b) How do rates of evaporation and condensation change initially?
(c) What happens when equilibrium is restored finally and what will be the final vapour pressure?

Ans. (a) Initially the vapour pressure will increase.
(b) The rate of evaporation will remain constant at constant temperature in closed vessel. However, rate of condensation will be low initially because there are lesser number of molecules per unit volume in the vapour phase. Therefore, the number of collisions per unit volume with the liquid surface decreases.
(c) When equilibrium is restored, rate of evaporation becomes equal to rate of condensation. The final vapour pressure will be same as it was originally.

Q.2. What is K_c for the following equilibrium when the equilibrium concentration of each substance is: $[SO_2] = 0.60M$, $[O_2] = 0.82M$ and $[SO_3] = 1.90\,M$?

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Ans.
$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(1.90)^2}{(0.60)^2 \times (0.82)}$$
$$= 12.229\,L\ mol^{-1}$$

Q.3. At a certain temperature and total pressure of 10^5Pa, iodine vapour contains 40% by volume of I atoms

$$I_2(g) \rightleftharpoons 2I(g)$$

Calculate K_p for the equilibrium.

Ans. *Refer Solved Example 14 (Page 22).*

Q.4. Write the expression for the equilibrium constant, K_c for each of the following reactions:

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

(ii) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

(iii) $CH_3COOC_2H_5(aq) + H_2O \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$

(iv) $Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$

(v) $I_2(s) + 5F_2 \rightleftharpoons 2IF_5$

Ans. *Refer Solved Example 11 (Page 17).*

Q.5. Find out the value of K_c for each of the following equilibria from the value of K_p:

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$; **$K_p = 1.8 \times 10^{-2}$ at 500 K**

(ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; **$K_p = 167$ at 1073 K**

Ans. $2NO\,Cl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

$K_p = 1.8 \times 10^{-2}$ at 500 K

$\Delta n = 3 - 2 = 1$

$K_c = K_p(RT)^{-\Delta n_g}$

$= 1.8 \times 10^{-2}\,(0.0831 \times 500)^{-1} = 4.33 \times 10^{-4}$

(ii) $\Delta n = 1 - 0 = 1$

$K_c = K_p(RT)^{-\Delta n_g}$

$= 167 \times (0.0831 \times 1073)^{-1} = \mathbf{1.87}$.

Q.6. For the following equilibrium, $K_c = 6.3 \times 10^{14}$ at 1000 K

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$$

Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c, for the reverse reaction ?

Ans.
$$K_{c(forward)} = 6.3 \times 10^{14}$$
$$K_{c(reverse)} = \frac{1}{K_{c(forward)}} = \frac{1}{6.3 \times 10^{14}}$$
$$= 1.59 \times 10^{-15}$$

Q.7. Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?

Ans. For the concentration of pure solid or pure liquid,

$$[\text{Solid}] \text{ or } [\text{liquid}] = \frac{\text{No. of moles}}{\text{Volume in L}}$$
$$= \frac{\text{Mass/Molar mass}}{\text{Volume}}$$
$$= \frac{\text{Mass}}{\text{Volume}} \times \frac{1}{\text{Molar mass}}$$
$$= \frac{\text{Density}}{\text{Molar mass}}$$

Since density of pure solids and liquids is constant at constant temperature and molar mass is also constant, therefore, their molar concentrations are constant and are not included in the equilibrium constant.

Q.8. Reaction between N_2 and O_2 takes place as follows:

$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$$

If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of equilibrium mixture.

Ans. *Refer Solved Example 20 (Page 24).*

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Q.9. Nitric oxide reacts with Br_2 and gives nitrosyl bromide as per reaction given below:

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

When 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and Br_2.

Ans. *Refer Solved Example 28 (Page 26).*

Q.10. At 450K, $K_p = 2.0 \times 10^{10}$/bar for the given reaction at equilibrium.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What is K_c at this temperature ?

Ans. For the reaction,

$$\Delta n_g = 2 - (2 + 1) = -1$$

$$K_p = K_c (RT)^{\Delta n_g}$$

$$K_c = K_p (RT)^{-\Delta n_g}$$

$$= (2.0 \times 10^{10}\ bar^{-1}) \times (0.0831\ L\ bar\ K^{-1}\ mol^{-1} \times 450\ K)^1$$

$$= 7.48 \times 10^{11}\ L\ mol^{-1}$$

Q.11. A sample of HI(*g*) is placed in a flask at a pressure of 0.2 atm. At equilibrium the partial pressure of HI(*g*) is 0.04 atm. What is K_p for the given equilibrium?

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Ans. *Refer Solved Example 29 (Page 27).*

Q.12. 13.8 g of N_2O_4 was placed in a 1L reaction vessel at 400 K and allowed to attain equilibrium :

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

The total pressure at equilibrium was found to be 9.15 bar. Calculate K_c, K_p and partial pressure at equilibrium.

Ans. *Refer Solved Example 26 (Page 26).*

Q13. The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

Ans. $4NO(g) + 6\,H_2O(g) \rightleftharpoons 4\,NH_3(g) + 5O_2(g)$

Q.14. One mole of H_2O and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation,

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Calculate the equilibrium constant for the reaction.

Ans. *Refer Solved Example 15 (Page 23)*

Q.15. At 700 K, equilibrium constant for the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is 54.8. If 0.5 mol L^{-1} of HI(*g*) is present at equilibrium at 700 K, what are the concentration of $H_2(g)$ and $I_2(g)$ assuming that we initially started with HI(*g*) and allowed it to reach equilibrium at 700K ?

Ans.

	$2HI(g)$	$\rightleftharpoons H_2(g)$	+ I_2
At equi	0.5	x	x

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{54.8}$$

$$\frac{x^2}{(0.5)^2} = \frac{1}{54.8}$$

$$x^2 = \frac{0.25}{54.8} = 4.56 \times 10^{-3}.$$

$$x = 0.068$$

$$[H_2] = [I_2] = 0.068\ mol\ L^{-1}$$

Q.16. What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M?

$$2ICl(g) \rightleftharpoons I_2(g) + Cl_2(g);\ K_c = 0.14$$

Ans. Let at equilibrium, $[I_2] = [Cl_2] = x$ mol L^{-1}

	$2ICl(g)$	$\rightleftharpoons I_2(g)$	+ $Cl_2(g)$
Initial conc.	0.78 M	0	0
At equ.	$0.78 - 2x$	x	x

$$K_c = \frac{[I_2][Cl_2]}{[ICl]^2}$$

$$0.14 = \frac{x \times x}{(0.78 - 2x)^2}$$

or $$x^2 = 0.14(0.78 - 2x)^2$$

or $$\frac{x}{(0.78 - 2x)} = \sqrt{0.14} = 0.374$$

or $$x = 0.292 - 0.748\,x$$

$$1.748\,x = 0.292$$

$$\therefore \quad x = 0.167$$

Thus, at equilibrium,

$[I_2] = 0.167$ M, $[Cl_2] = 0.167$ M,

$[ICl] = 0.78 - 2 \times 0.167 = 0.446$ M

Q.17. $K_p = 0.04$ atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

Ans.

	$C_2H_6(g)$	$\rightleftharpoons C_2H_4(g)$	+ $H_2(g)$
Initial conc.	4.0 atm	0	0
At equi.	$4 - p$	p	p

$$K_p = \frac{p \times p}{4 - p} = 0.04$$

$$p^2 = 0.16 - 0.04\,p$$

Solving for p, we get $p = 0.38$

$\therefore$ Conc of C_2H_6 at eq. $= 4 - 0.38 =$ **3.62 atm**

Q.18. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If value of K_c is 8.3×10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium?

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Ans.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Let concentration of PCl_3 and Cl_2 at equilibrium be x molL^{-1}.

$$[PCl_5] = 0.05$$

$$K_c = 8.3 \times 10^{-3}$$

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$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$8.3 \times 10^{-3} = \frac{x \times x}{0.05}$$

$$x = 2.04 \times 10^{-2} \text{ mol L}^{-1}$$

$\therefore$ $[PCl_3] = \mathbf{2.04 \times 10^{-2} \text{ mol L}^{-1}}$

$[Cl_2] = \mathbf{2.04 \times 10^{-2} \text{ mol L}^{-1}}$.

Q.19. Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as :

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

(*i*) Write the concentration ratio (reaction quotient), Q_c, for this reaction (note: water is not in excess and is not a solvent in this reaction).

(*ii*) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(*iii*) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached ?

Ans. (*i*) $$Q_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

(*ii*)

	CH_3COOH	+ C_2H_5OH	$\rightleftharpoons$ $CH_3COOC_2H_5$	+ H_2O
Initial conc	1.00	0.18	0	0
At equi.	1 – 0.171 = 0.829 mol	0.18 – 0.171 = 0.009 mol	0.171 mol	0.171 mol
Molar conc.	0.829/V	0.009/V	0.171/V	0.171/V

$$K_c = \frac{(0.171/V) \times (0.171/V)}{(0.829/V) \times (0.009/V)} = \mathbf{3.92}$$

(*iii*)

	CH_3COOH	+ C_2H_5OH	$\rightleftharpoons$ $CH_3COOC_2H_5$	+ H_2O
Initial conc.	1.00 mol	0.500 mol		
At equi	1 – 0.214 = 0.786 mol	0.500 – 0.214 = 0.286 mol	0.214 mol	0.214 mol

$$Q_c = \frac{(0.214/V) \times (0.214/V)}{(0.786/V) \times (0.286/V)} = \mathbf{0.204}$$

Since, $Q_c \neq K_c$, equilibrium has not been reached.

Q.20. One of the reaction that takes place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and CO_2.

$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$;

$K_p = 0.265$ atm at 1050 K

What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are: $p_{co} = 1.4$ atm and $p_{CO_2} = 0.80$ atm?

Ans. $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$

Initial pressure: 1.4 atm, 0.80 atm

$$Q_p = \frac{p_{CO_2}}{p_{CO}} = \frac{0.80}{1.4} = 0.571$$

Since $Q_p > K_p$; the reaction will move in the backward direction. Therefore, pressure of CO_2 will decrease and that of CO will increase to attain equilibrium.

If p is the decrease in pressure of CO_2, then increase in pressure of CO = p

$\therefore$ At equilibrium $p_{CO_2} = (0.80 - p)$ atm

$p_{CO} = (1.4 + p)$ atm

$$K_p = \frac{0.80 - p}{1.4 + p} = 0.265$$

or $0.265\,(1.4 + p) = 0.80 - p$

or $0.371 + 0.265\,p = 0.80 - p$

or $1.265\,p = 0.429$

or $$p = \frac{0.429}{1.265} = 0.339 \text{ atm}$$

At equilibrium :

$p_{CO} = 1.4 + 0.339 = \mathbf{1.739}$ atm

$p_{CO_2} = 0.80 - 0.339 = \mathbf{0.461}$ atm

Q21. Equilibrium constant, K_c for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500 K is 0.061.

At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium? If not, in which direction does the reaction tend to proceed to reach equilibrium?

Ans. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$Q = \frac{(0.50)^2}{(3.0) \times (2.0)^3} = 0.0104$$

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Since $Q_c \neq K_c$, the reaction is not in equilibrium.
As $Q_c < K_c$ the reaction will proceed to form more products i.e., in forward direction.

Q.22. Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium:

$$2BrCl\,(g) \rightleftharpoons Br_2\,(g) + Cl_2(g)$$

for which $K_c = 32$ at 500 K. If initially pure BrCl is present at concentration of 3.3×10^{-3} mol L^{-1}, what is its molar concentration in the mixture at equilibrium?

Ans.

	$2BrCl\,(g)$	$\rightleftharpoons$	$Br_2\,(g)$	+	$Cl_2(g)$
Initial conc.	3.30×10^{-3}				
At equi.	$(3.30 \times 10^{-3} - x)$		$x/2$		$x/2$

where x is the amount of BrCl dissociated.

$$K_c = \frac{[Br_2][Cl_2]}{[BrCl]^2}$$

$$= \frac{x/2 \times x/2}{(3.30 \times 10^{-3} - x)^2} = 32$$

Solving

$$x = 3.00 \times 10^{-3}$$

$\therefore$ At equilibrium [BrCl]

$$= 3.30 \times 10^{-3} - 3.00 \times 10^{-3}$$

$$= 0.30 \times 10^{-3}$$

or $= \mathbf{3.0 \times 10^{-4}\ mol\ L^{-1}}$

Q.23. At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass

$$C(s) + CO_2\,(g) \rightleftharpoons 2\,CO\,(g)$$

Calculate K_c for this reaction at the above temperature.

Ans. *Refer Solved Example 22 (Page 25).*

Q.24. Calculate (*a*) $\Delta G^\ominus$ and (*b*) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298K

$$NO(g) + \frac{1}{2}\,O_2\,(g) \rightleftharpoons NO_2(g)$$

where

$\Delta_f G^\ominus\,(NO_2) = 52.0$ kJ/mol
$\Delta_r G^\ominus\,(NO) = 87.0$ kJ/mol,
$\Delta_r G^\ominus\,[O_2] = 0$ kJ/mol

Ans. *Refer Solved Example 35. (Page 30)*

Q.25. Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?

(*a*) $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2(g)$

(*b*) $CaO\,(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

(*c*) $3Fe\,(s) + 4H_2O\,(g) \rightleftharpoons Fe_3O_4\,(s) + 4H_2(g)$

Ans. *Refer Conceptual Qs. 1 Q.18 (page 39).*

Q.26. Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction.

(*i*) $COCl_2(g) \rightleftharpoons CO\,(g) + Cl_2(g)$

(*ii*) $CH_4(g) + 2\,S_2\,(g) \rightleftharpoons CS_2(g) + 2H_2S\,(g)$

(*iii*) $CO_2\,(g) + C\,(s) \rightleftharpoons 2CO\,(g)$

(*iv*) $2H_2\,(g) + CO\,(g) \rightleftharpoons CH_3OH\,(g)$

(*v*) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2(g)$

(*vi*) $4\,NH_3(g) + 5O_2(g) \rightleftharpoons 4NO\,(g) + 6\,H_2O(g)$

Ans. *Refer Conceptual Qs. 1 Q.19 (page 39).*

Q.27 The equilibrium constant for the following reaction is 1.6×10^5 at 1024 K

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr\,(g)$$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

Ans. *Refer Solved Example 18. (Page 23)*

Q.28. Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:

$$CH_4\,(g) + H_2O\,(g) \rightleftharpoons CO(g) + 3\,H_2(g)$$

(*a*) Write an expression for K_p for the above reaction.

(*b*) How will the values of K_p and composition of equilibrium mixture be affected by

(*i*) increasing the pressure

(*ii*) increasing the temperature

(*iii*) using a catalyst?

Ans. *Refer Solved Example 37 (Page 36).*

Q.29. Describe the effect of

(*a*) addition of H_2 (*b*) addition of CH_3OH

(*c*) removal of CO (*d*) removal of CH_3OH

on the equilibrium of the reaction:

$$2H_2(g) + CO\,(g) \rightleftharpoons CH_3OH(g)$$

Ans. (*a*) Equilibrium will shift in the *forward direction*
(*b*) Equilibrium will shift in the *backward direction*
(*c*) Equilibrium will shift in the *backward direction*
(*d*) Equilibrium will shift in the *forward direction*

Q.30 At 473K, equilibrium K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)\ \Delta_r H^\ominus = 124.0\ kJ\ mol^{-1}$$

(*a*) Write an expression for K_c for the reaction.

(*b*) What is the value of K_c for the reverse reaction at the same temperature?

(*c*) What would be the effect on K_c if (*i*) more PCl_5 is added (*ii*) pressure is increased (*iii*) the temperature is increased?

Ans. *Refer Conceptual Qs. 1 , Q.20 (Page 39).*

Q.31. Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H_2. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $p_{CO} = p_{H2O} = 4.0$ bar, what will be the partial pressure of H_2 at equilibrium? $K_p = 10.1$ at 400°C

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Ans. Suppose the partial pressure of H_2 at equilibrium = p bar

	$CO(g)$ +	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$ +	$H_2(g)$
Initial pressure	4.0 bar	4.0 bar		0	0
At equi	$(4-p)$ bar	$(4-p)$ bar		p bar	p bar

$$K_p = \frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}}$$

$$= \frac{p \times p}{(4-p) \times (4-p)} = 0.1$$

$$\frac{p}{4-p} = \sqrt{0.1} = 0.316$$

$$p = 1.264 - 0.316\,p$$

or $1.316\,p = 1.264$

$\therefore$ p = **0.96 bar**

Q.32. Predict which of the following reaction will have appreciable concentration of reactants and products:

(a) $Cl_2(g) \rightleftharpoons 2Cl\,(g)$ $K_c = 5 \times 10^{-39}$

(b) $Cl_2(g) + 2NO\,(g) \rightleftharpoons 2NOCl\,(g)$ $K_c = 3.7 \times 10^8$

(c) $Cl_2(g) + 2NO_2(g) \rightleftharpoons 2NO_2Cl(g)$; $K_c = 1.8$

Ans. *Refer Conceptual Qs. 1 Q.21 (Page 40).*

Q.33. The value of K_c for the reaction

$3O_2\,(g) \rightleftharpoons 2O_3\,(g)$ **is** 2.0×10^{-50}

at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2}, what is the concentration of O_3?

Ans. *Refer Conceptual Qs. 1 , Q. 22 (Page 40).*

Q.34. The reaction,

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

is at equilibrium at 1300 K in a 1L flask. It also contains 0.30 mol of CO, 0.10 mol of H_2 and 0.02 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.

Ans.

$$K_c = \frac{[CH_4]\,[H_2O]}{[CO]\,[H_2]^3}$$

$$3.90 = \frac{[CH_4] \times 0.02}{(0.30)\,(0.10)^3}$$

or

$$[CH_4] = \frac{3.90 \times 0.30 \times (0.10)^3}{0.02}$$

$$= 5.85 \times 10^{-2}\ M$$

Q.35. What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species :

HNO_2, CN^-, $HClO_4$, F^-, OH^-, CO_3^{2-}, and S^{2-}

Ans. An acid-base pair which differs by a proton is called conjugate acid-base pair.

HNO_2 : NO_2^-, CN^- : HCN

$HClO_4$: ClO_4^-, F^- : HF

OH^- : H_2O (acid) or O^{2-} (base); CO_3^{2-} : HCO_3^-

S^{2-} : HS^-

Q.36. Which of the following are Lewis acids ? H_2O, BF_3 H^+ and NH_4^+

Ans. Lewis acids are: BF_3, H^+, NH_4^+

Q.37. What will be the conjugate bases for the Bronsted acids : HF, H_2SO_4 and HCO_3^-?

Ans. Conjugate bases : F^-, HSO_4^-, CO_3^{2-}

Q.38. Write the conjugate acids for the following Bronsted bases: NH_2^-, NH_3 and $HCOO^-$.

Ans. Conjugate acids: NH_3, NH_4^+, HCOOH

Q.39. The species: H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and base.

Ans. *Refer Solved Example 40 (Page 48)*

Q.40. Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base: (a) OH^- (b) F^- (c) H^+ (d) BCl_3.

Ans. *Refer Solved Example 41 (Page 48).*

Q.41. The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3}M. What is its pH?

Ans. *Refer Solved Example 42 (Page 52).*

Q.42. The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

Ans. $-\log [H^+] = 3.76$ or $\log [H^+] = -3.76$

$\therefore [H^+] = 1.73 \times 10^{-4}$M

Q.43. The ionization constant of HF, HCOOH and HCN at 298 K are 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate bases.

Ans. *(i)* K_a (HF) $= 6.8 \times 10^{-4}$

$$K_b(F^-) = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11}$$

(ii) K_a (HCOOH) $= 1.8 \times 10^{-4}$

$$K_b(HCOO^-) = \frac{1 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$$

(iii) $K_a(HCN) = 4.8 \times 10^{-9}$

$$K_b(CN^-) = \frac{1 \times 10^{-14}}{4.8 \times 10^{-9}} = 2.08 \times 10^{-6}$$

Q.44. The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01 M in sodium phenolate?

Ans. *Refer Solved Example 76 (Page 68).*

Q.45. The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ion in its 0.1M solution. How will this concentration be affected if the solution is 0.1M in HCl also? If the second dissociation constant of H_2S is 1.2×10^{-13}, calculate the concentration of S^{2-} under both conditions.

Ans. *Refer Solved Example 74 (Page 67).*

Q.46. The ionization constant of acetic acid is 1.74×10^{-5}. Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

Ans. If α is the degree of dissociation, then at equilibrium

	CH_3COOH	$\rightleftharpoons$	CH_3COO^- +	H^+
Initial Conc.	c		0	0
At equi.	$c(1-\alpha)$		$c\alpha$	$c\alpha$

$$K_a = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]}$$

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or $= \frac{(c\alpha)\times(c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \approx c\alpha^2$

$\therefore \quad \alpha = \sqrt{\frac{ka}{c}} = \sqrt{\frac{1.74\times10^{-5}}{0.05}} = 1.865\times10^{-2}$

$[H^+] = c\alpha = 0.05 \times 1.865 \times 10^{-2} = 9.33 \times 10^{-4}$ M

Now, $[CH_3COO^-] = [H^+] = 9.33 \times 10^{-4}$ M

$pH = -\log(9.33\ 5\ 10^{-4})$

$= 4 - 0.9699 = 3.03$

Q.47. It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pK_a.

Ans. *Refer Solved Example 60 (Page 59).*

Q.48. Assuming complete dissociation, calculate the pH of the following solutions:

(*a*) 0.003 M HCl (*b*) 0.005 M NaOH

(*c*) 0.002 M HBr (*d*) 0.002 M KOH

Ans. *Refer Solved Example 53 (Page 57).*

Q.49. Calculate the pH of the following solutions:

(*a*) 2 g of TlOH dissolved in water to give 2 litre of solution.

(*b*) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.

(*c*) 0.3 g of NaOH dissolved in water to give 200 mL of solution.

(*d*) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of solution.

Ans. *Refer Solved Example 54 (Page 57).*

Q.50. The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a of bromoacetic acid.

Ans. *Refer Solved Example 56 (Page 58).*

Q.51. The pH 0.005M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pK_b.

Ans. $Cod. + H_2O \rightleftharpoons Cod\,H^+ + OH^-$

$pH = 9.95$, $pOH = 14 - 9.95 = 4.05$

$\therefore -\log[OH^-] = 4.05$

$\log[OH^-] = -4.05$ or $= 5.95$

$\therefore \quad [OH^-] = 8.913 \times 10^{-5}$

$$K_b = \frac{[Cod\,H^+][OH^-]}{[Cod]} = \frac{[OH^-]^2}{[Cod]}$$

$$= \frac{(8.913\times10^{-5})^2}{5\times10^{-3}} = 1.588 \times 10^{-6}$$

$pK_b = -\log(1.588 \times 10^{-6}) = -(-6 + 0.200)$

$= 5.8$

Q.52. What is the *p*H of 0.001M aniline solution? The ionization constant of aniline is 4.3×10^{-10}. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.

Ans. *Refer Solved Example 71 (Page 63).*

Q.53. Calculate the degree of ionization of 0.05 M acetic acid if its pK_a value is 4.74. How is the degree of dissociation affected when its solution also contains (a) 0.01M (b) 0.1M in HCl?

Ans. *Refer Solved Example 75 (Page 67).*

Q.54. The ionization constant of dimethylamine is 5.4×10^{-4}. Calculate its degree of ionization in its 0.02M solution. What percentage of dimethylamine is ionized if the solution is also 0.1M in NaOH?

Ans. $\alpha = \sqrt{\frac{K_b}{c}}$

$K_b = 5.4 \times 10^{-4}$, $c = 0.02$M

$\therefore \quad \alpha = \sqrt{\frac{(5.4\times10^{-4})}{2\times10^{-2}}} = 0.164$

Let the amount of dimethylamine dissociated in the presence of 0.1M NaOH be x.

$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$

Initial	0.02			
After dissociation	$0.02 - x \approx 0.02$		x	$0.1 + x \approx 0.1$

$$K_b = \frac{x\times(0.1+x)}{(0.02-x)} \approx \frac{x\times0.1}{0.02}$$

or $\quad x = \frac{5.4\times10^{-4}\times0.02}{0.1}$

$= 1.08 \times 10^{-4}$

$\therefore$ % of dimethylamine ionized

$$= \frac{1.08\times10^{-4}}{0.02} \times 100 = 0.54\%$$

Q.55. Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:

(*a*) Human muscle-fluid, 6.83

(*b*) Human stomach fluid, 1.2

(*c*) Human blood, 7.38

(*d*) Human saliva, 6.4.

Ans. (*i*) $-\log[H_3O^+] = 6.83$

$[H_3O^+] = 1.48 \times 10^{-7}$M

(*ii*) $-\log[H_3O^+] = 1.2$

$[H_3O^+] = 6.31 \times 10^{-2}$ M

(*iii*) $-\log[H_3O^+] = 7.38$

$[H_3O^+] = 4.169 \times 10^{-8}$M

(*iv*) $-\log[H_3O^+] = 6.4$

$[H_3O^+] = 3.981 \times 10^{-7}$M

Q.56. The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each.

Ans. (*i*) milk : $-\log[H_3O^+] = 6.8$

$[H_3O^+] = 1.58 \times 10^{-7}$

(*ii*) black coffee : $-\log[H_3O^+] = 5.0$

$[H_3O^+] = 1 \times 10^{-5}$

(*iii*) tomato juice : $-\log[H_3O^+] = 4.2$

$[H_3O^+] = 6.31 \times 10^{-5}$

(*iv*) Lemon juice : $-\log[H_3O^+] = 2.2$

$[H_3O^+] = 6.31 \times 10^{-3}$ M

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(*v*) egg white : $-\log[H_3O^+] = 7.8$

$[H_3O^+] = 1.58 \times 10^{-8}$

Q.57. If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

Ans. $[KOH] = \frac{0.561}{56} \times \frac{1000}{200} = 0.050M$

$KOH = K^+ + OH^-$

$[K^+] = 0.05\ M, [OH^-] = 0.05\ M$

$[H^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{0.05} = 2.0 \times 10^{-13}$

$pH = -\log(2.0 \times 10^{-13}) = \mathbf{12.699}$

Q.58. The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

Ans. *Refer Solved Example 52 (Page 57).*

Q.59. The ionization constant of propanoic acid is 1.32×10^{-5}. Calculate the degree of ionization of the acid in its 0.05M solution and also its pH. What will be its degree of ionization if the solution is 0.01M in HCl also?

Ans. If α is the degree of dissociation,

$$\alpha = \sqrt{\frac{K_a}{c}}$$

$$= \sqrt{\frac{1.32 \times 10^{-5}}{0.05}} = 1.62 \times 10^{-2}$$

$[H^+] = c\alpha = 0.05 \times 1.62 \times 10^{-2} = 8.12 \times 10^{-4}$

$pH = -\log [H^+]$

$= -\log (8.12 \times 10^{-4}) = 3.09.$

In the presence of 0.01 M HCl,

$\alpha = \mathbf{1.32 \times 10^{-3}}$.

Q.60. The pH of 0.1M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

Ans. *Refer Solved Example 62 (Page 60).*

Q61. The ionization constant of nitrous acid is 4.5×10^{-4}. Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

Ans. $pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \log c$

$pK_a = -\log K_a = -\log (4.5 \times 10^{-4})$

$= -(0.65 - 4) = 3.35$

$\therefore \quad pH = \frac{1}{2}(14) + \frac{1}{2}(3.35) + \log 0.04$

$= 7 + 1.675 - 1.39 = \mathbf{7.285}$

$h = \sqrt{\frac{K_w}{K_a.c}}$

$= \sqrt{\frac{1 \times 10^{-14}}{4.5 \times 10^{-4} \times 0.04}} = \mathbf{2.35 \times 10^{-5}}$

Q. 62. A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine.

Ans. *Refer Solved Example 84 (Page 77)*

Q63. Predict if the solutions of the following salts are neutral, acidic or basic:

NaCl, KBr, NaCN, NH_4NO_3, $NaNO_2$ and KF

Ans. Acidic, basic or neutral character of the salt can be decided on the basis whether they are salts of strong or weak acids or bases.

(*i*) NaCN, $NaNO_2$, KF are basic because they are the salts of strong base and weak acids.

(*ii*) NH_4NO_3 is acidic because it is a salt of strong acid and weak base.

(*iii*) NaCl, KBr are neutral because they are salts of strong acids and strong bases.

Q64. The ionization constant of chloroacetic acid is 1.35×10^{-3}. What will be the pH of 0.1 M acid and its 0.1 M sodium salts solution ?

Ans. *Refer Solved Example 86 (Page 77).*

Q65. Ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature?

Ans. *Refer Conceptual Qs. 2 , Q.9 (Page 70).*

Q66. Calculate the pH of the resultant mixtures:

(a) 10 mL of 0.2M $Ca(OH)_2$ + 25 mL of 0.1M HCl

(b) 10 mL of 0.01M H_2SO_4 + 10 mL of 0.01M $Ca(OH)_2$

(c) 10 mL of 0.1M H_2SO_4 + 10mL of 0.1M KOH

Ans. (a) 10 mL of 0.2 M $Ca(OH)_2 = \frac{10 \times 0.2}{1000}$

$= 2 \times 10^{-3}$ moles

25 mL of 0.1 M HCl $= \frac{25 \times 0.2}{1000}$

$= 2.5 \times 10^{-3}$ moles

$Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$

1 mole of $Ca(OH)_2$ reacts with 2 moles of HCl

2.5×10^{-3} moles of HCl will react with 1.25×10^{-3} mole of $Ca(OH)_2$.

$\therefore$ $Ca(OH)_2$ left $= 2 \times 10^{-3} - 1.25 \times 10^{-3}$

$= 0.75 \times 10^{-3}$mole

Total volume $= 10 + 25 = 35$ mL

Molarity of $Ca(OH)_2 = \frac{0.75 \times 10^{-3} \times 1000}{35}$

$= 0.0214$ M

$[OH^-] = 2 \times 0.0214 = 4.28 \times 10^{-2}$M

$pOH = -\log (4.28 \times 10^{-2}) = -(-2 + 0.6314)$

$= \mathbf{1.368}$

$pH = 14 - 1.368 = 12.632$

(*b*) 10 mL of 0.01 $H_2SO_4 = \frac{10 \times 0.01}{1000}$

$= 0.1 \times 10^{-3}$ mole

10 mL of 0.01 M $Ca(OH)_2 = \frac{10 \times 0.01}{1000}$

$= 0.1 \times 10^{-3}$ mole

$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$

1 mole of $Ca(OH)_2$ reacts with 1 mole of H_2SO_4

$\therefore 0.1 \times 10^{-3}$ mole of $Ca(OH)_2$ will react completely with 0.1×10^{-3} mole of H_2SO_4.

The resulting solution will be neutral with pH = 7.0

(*c*) 10 mL of 0.1 M $H_2SO_4 = \frac{10 \times 0.1}{1000}$

$= 1 \times 10^{-3}$mole

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$2\,KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$

1 mole of KOH reacts with 0.5 mole of H_2SO_4

$\therefore$ 1×10^{-3} mole of KOH will react with 0.5×10^{-3} mole of H_2SO_4

H_2SO_4 left $= (1 - 0.5) \times 10^{-3} = 0.5 \times 10^{-3}$

Volume of solution = 10 + 10 = 20 mL

$$\text{Molarity of solution} = \frac{0.5 \times 10^{-3} \times 1000}{20}$$

$$= 2.5 \times 10^{-2}\,M$$

$\therefore$ $[H^+] = 2 \times 2.5 \times 10^{-2}M = 5.0 \times 10^{-2}M$

$pH = -\log(5.0 \times 10^{-2}) = -(-2 + 0.699)$

= 1.3

Q. 67. Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298K from their solubility product constants given below:
$Ag_2CrO_4 = 1.1 \times 10^{-12}$, $BaCrO_4 = 1.2 \times 10^{-10}$
$Fe(OH)_3 = 1.0 \times 10^{-38}$, $PbCl_2 = 1.6 \times 10^{-5}$,
$Hg_2I_2 = 4.5 \times 10^{-29}$
Determine also the molarities of individual ions.

Ans. (*i*) Silver chromate, Ag_2CrO_4

$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$[Ag^+] = 2s, CrO_4^{2-} = s$

$K_{sp} = (2s)^2 (s) = 4s^3$

$\therefore$ $4s^3 = 1.1 \times 10^{-12}$

$$s = \left(\frac{1.1 \times 10^{-12}}{4}\right) = 6.5 \times 10^{-5}$$

$[Ag^+] = 1.30 \times 10^{-4}M,$

$[CrO_4^{2-}] = 6.5 \times 10^{-5}M$

(*ii*) Barium chromate, $BaCrO_4$

$BaCrO_4 \rightleftharpoons Ba^{2+} + CrO_4^{2-}$

$[Ba^{2+}] = s, CrO_4^{2-} = s$

$K_{sp} = (s)(s) = s^2$

$s^2 = 1.2 \times 10^{-10}$

$s = (1.2 \times 10^{-10})^{1/2} = 1.09 \times 10^{-5}M$

$[Ba^{2+}] = 1.09 \times 10^{-5}M,$

$[CrO_4^{2-}] = 1.09 \times 10^{-5}M$

(*iii*) Ferric hydroxide, $Fe(OH)_3$

$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$

$[Fe^{3+}] = s, [OH^-] = 3s$

$K_{sp} = (s)(3s)^3 = 27s^4$

$27s^4 = 1.0 \times 10^{-38}$

$$s = \left(\frac{1.0 \times 10^{-38}}{27}\right)^{1/4} = 1.38 \times 10^{-10}M$$

$[Fe^{3+}] = 1.38 \times 10^{-10}\,M,$

$[OH^-] = 4.14 \times 10^{-10}M$

(*iv*) Lead chloride, $PbCl_2$

$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$

$[Pb^{2+}] = s, [Cl^-] = 2s$

$K_{sp} = (s) \times (2s)^2 = 4s^3$

$4s^3 = 1.6 \times 10^{-5}$

$$s = \left(\frac{1.6 \times 10^{-5}}{4}\right)^{1/3} = 1.59 \times 10^{-2}M$$

$[Pb^{2+}] = 1.59 \times 10^{-2}M$

$[Cl^-] = 3.18 \times 10^{-2}M$

(*v*) Mercurous iodide, Hg_2I_2

$Hg_2I_2 \rightleftharpoons 2Hg^+ + 2I^-$

$[Hg^+] = 2s, [I^-] = 2s$

$K_{sp} = (2s)^2 (2s)^2$

$= 16s^4$

$16s^4 = 4.5 \times 10^{-29}$

$$s = \left(\frac{4.5 \times 10^{-29}}{16}\right)^{1/4} = 4.09 \times 10^{-8}\,M$$

$[Hg^+] = 8.18 \times 10^{-8}M,$

$[I^-] = 8.18 \times 10^{-8}\,M.$

Q.68. The solubility product constants of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

Ans. *Refer Solved Example 101 (Page 85).*

Q.69. Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$)

Ans. Conc. of $NaIO_3$ after mixing

$$= \frac{0.002}{2} = 0.001\,M$$

Conc. of $Cu(ClO_3)_2$ after mixing

$$= \frac{0.002}{2} = 0.001\,M$$

$NaIO_3 \rightleftharpoons Na^+ + IO_3^-$

$[IO_3^-] = 0.001\,M$

$Cu(ClO_3)_2 \rightleftharpoons Cu^{2+} + 2\,ClO_3^-$

$[Cu^{2+}] = 0.001M$

Ionic product of $Cu(IO_3)_2$

$= [Cu^{2+}][IO_3^-]^2$

$= (0.001) \times (0.001)^2$

$= 1 \times 10^{-9}$

Since ionic product is less than K_{sp} (7.4×10^{-4}), no precipitation will occur.

Q70. The ionization constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water ?

Ans. *Refer Solved Example 113 (Page 88).*

Q71. What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, $K_{sp} = 6.3 \times 10^{-18}$).

Ans. *Refer Solved Example 110 (Page 87).*

Q72. What is the minimum volume of water required to dissolve 1g of calcium sulphate at 298 K? (For calcium sulphate, K_{sp} is 9.1×10^{-6}).

Ans. *Refer Solved Example 103 (Page 86).*

Q73. The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following: $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$ in which of these solutions precipitation will take place?

Ans. *Refer Solved Example 111 (Page 88).*

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NCERT Exemplar Problems

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 153.*

Short Answer Questions *Carrying 2 or 3 marks*

Q. 1. The ionisation of hydrochloric acid in water is given below :
$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$
Label two conjugate acid-base pairs in this ionisation.

Ans. HCl(acid), Cl^- (conjugate base)
H_2O(base), H_3O^+ (conjugate acid)

Q. 2. The aqueous solution of sugar does not conduct electricity. However, when sodium chloride is added to water, it conducts electricity. How will you explain this statement on the basis of ionisation and how is it affected by concentration of sodium chloride ?

Ans. (*i*) Sugar is non-electrolyte and does not ionise in water but NaCl ionises completely in water and produces Na^+ and Cl^- ions, which help in conduction of electricity.
(*ii*) Conductance increases with increase in concentration of NaCl due to release of more Na^+ and Cl^- ions.

Q. 3. BF_3 does not have proton but still acts as an acid and reacts with NH_3, Why is it so ? What type of bond is formed between the two ?

Ans. BF_3 acts as a Lewis acid because it is electron deficient compound. It forms a coordinate bond with NH_3 which acts as a base as :

$$H_3N : \rightarrow BF_3.$$

Q. 4. Ionisation constant of a weak base MOH, is given by the expression

$$K_b = \frac{[M^+][OH^-]}{[MOH]}$$

Values of ionisation constant of some weak bases at a particular temperature are given below :

Base	*Dimethylamine*	*Urea*	*Pyridine*	*Ammonia*
K_b	5.4×10^{-4}	1.3×10^{-14}	1.77×10^{-9}	1.77×10^{-5}

Arrange the bases in decreasing order of the extent of their ionisation at equilibrium. Which of the above base is the strongest ?

Ans. (*i*) Order of extent of ionisation at equilibrium is :
Dimethylamine > Ammonia > Pyridine > Urea
(*ii*) Since dimethylamine will ionise to the maximum extent it is the strongest base.

Q. 5. Conjugate acid of a weak base is always stronger. What will be the decreasing order of basic strength of the following conjugate bases ?
OH^-, RO^-, CH_3COO^-, Cl^-.

Ans. Conjugate acids of given bases are H_2O, ROH, CH_3COOH, HCl.
Their acidic strength is :

$$HCl > CH_3COOH > H_2O > ROH.$$

Hence, conjugate bases are in the order :

$$Cl^- < CH_3COO^- < OH^- < RO^-.$$

Q. 6. Arrange the following in increasing order of pH.
$KNO_3(aq)$, $CH_3COONa(aq)$, $NH_4Cl(aq)$, $C_6H_5COONH_4(aq)$.

Ans. KNO_3 neutral pH = 7, CH_3COONa (salt of weak acid and strong base), pH > 7, NH_4Cl (salt of weak base and strong acid), pH < 7, $C_6H_5COONH_4$ (both weak but NH_4OH is slightly stronger than C_6H_5COOH) pH close to 7 only slightly > 7.
Hence, order is $NH_4Cl < KNO_3 < C_6H_5COONH_4 < CH_3COONa$.

Q. 7. The value of K_c for the reaction
$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ is 1×10^{-4}
At a given time, the composition of reaction mixture is $[HI] = 2 \times 10^{-5}$ mol, $[H_2] = 1 \times 10^{-5}$ mol and $[I_2] = 1 \times 10^{-5}$ mol. In which direction will the reaction proceed ?

Ans. Reaction quotient, $Q = \frac{[H_2][I_2]}{[HI]^2} = \frac{(10^{-5})(10^{-5})}{(2 \times 10^{-5})^2} = 0.25.$

Since $Q > K_c$, the reaction will proceed in backward direction.

Q. 8. On the basis of the equation pH = – log[H^+]. The pH of 10^{-8} mol dm^{-3} solution of HCl should be 8. However, it is observed to be less than 7.0. Explain the reason.

Ans. pH of 10^{-8} MHCl is not 8 because the solution is very dilute. The concentration of H^+ ions is so low that H^+ ions produced from water cannot be neglected. *Refer Solved Example 65.* (*Page 60*).

Q. 9. pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained after diluting the given solution a 100 times ?

Ans. *Refer Conceptual Qs.* 2 , *Q. 12,* (*Page 70*).

Q. 10. A sparingly soluble salt gets precipitated only when the product of concentration of its ions in the solution (Q_{ip}) becomes greater than its solubility product. If the solubility of $BaSO_4$ in water is 8×10^{-4} mol dm^{-3}. Calculate its solubility in 0.01 mol dm^{-3} of H_2SO_4.

Ans. The solubility equilibrium is

$$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$$

Solubility of $BaSO_4 = 8 \times 10^{-4}$ mol dm^{-3}
$\therefore$ $[Ba^{2+}] = 8 \times 10^{-4}$ mol dm^{-3}
$[SO_4^{2-}] = 8 \times 10^{-4}$ mol dm^{-3}

$K_{sp} = [Ba^{2+}][SO_4^{2-}]$
$\therefore$ $K_{sp} = (8 \times 10^{-4})(8 \times 10^{-4})$
$= 64 \times 10^{-8}$

H_2SO_4 ionizes completely as :

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

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$\therefore$ $[SO_4^{2-}]$ produced from 0.01 mol dm^{-3} of H_2SO_4 = 0.01 M.

If x is the solubility of $BaSO_4$ in H_2SO_4, then

$$[Ba^{2+}] = x,\ [SO_4^{2-}] = x + 0.01$$

Since K_{sp} is constant for a given salt,

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$
$$= x(x + 0.01) = 64 \times 10^{-8}$$

or $x^2 + 0.01\,x - 64 \times 10^{-8} = 0$

Solving for x, we get $x = \mathbf{6 \times 10^{-4}\ mol\ dm^{-3}}$.

Q. 11. pH of 0.08 mol dm^{-3} HOCl solution is 2.85. Calculate its ionisation constant.

Ans. pH = 2.85 or $-\log [H^+] = 2.85$

or $\log [H^+] = -2.85 = \bar{3}.15$

$[H^+]$ = antilog $(\bar{3}.15)$

$= 1.413 \times 10^{-3}$

For weak acid, $HOCl \longrightarrow H^+ + OCl^-$

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]}$$
$$= \frac{(1.413 \times 10^{-3})^2}{0.08}$$
$$= \mathbf{2.496 \times 10^{-5}}.$$

Q. 12. Calculate the pH of a solution formed by mixing equal volumes of two solutions A and B of a strong acid having pH = 6 and pH = 4 respectively.

Ans. *Refer Solved Example 64 (Page 60).*

Q. 13. The solubility product of $Al(OH)_3$ is 2.7×10^{-11}. Calculate its solubility in gL^{-1} and also find out pH of this solution. (Atomic mass of Al = 27).

Ans. *Refer Solved Example 104. (Page 86)*

Q. 14. Calculate the volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution. (K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$, atomic mass of Pb = 207).

Ans. *Refer Solved Example 112. (Page 88)*

Q. 15. A reaction between ammonia and boron trifluoride is given below :

$$\mathbf{:NH_3 + BF_3 \longrightarrow H_3N : BF_3}$$

Identify the acid and base in this reaction. Which theory explains it ? What is the hybridisation of B and N in the reactants ?

Ans. NH_3 is a Lewis base and BF_3 is a Lewis acid. Lewis theory of acids and bases explains this.

B in BF_3 is sp^2 hybridised

N in NH_3 is sp^3 hybridised.

Q. 16. Following data is given for the reaction : $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Given that $\Delta_f H°[CaO(s)] = -635.1$ kJ mol^{-1}

$\Delta_f H°[CO_2(g)] = -393.5$ kJ mol^{-1}

$\Delta_f H°[CaCO_3(s)] = -1206.9$ kJ mol^{-1}

Predict the effect of temperature on the equilibrium constant of the above reaction.

Ans. $\Delta_r H° = \Delta_f H°(CaO) + \Delta_f H°(CO_2) - \Delta_f H°(CaCO_3)$

$= -635.1 + (-393.5) - (-1206.9)$

$= 178.3$ kJ mol^{-1}.

The reaction is endothermic. Hence according to Le-Chatelier principle, on increasing the temperature, the equilibrium will proceed in the forward direction.

Long Answer Questions *Carrying 5 marks*

Q. 17. How can you predict the following stages of a reaction by comparing the value of K_c and Q_c?

(*i*) Net reaction proceeds in the forward direction.

(*ii*) Net reaction proceeds in the backward direction.

(*iii*) No net reaction occurs.

Ans. (*i*) When $Q_c < K_c$ (*ii*) When $Q_c > K_c$

(*iii*) When $Q_c = K_c$

Q. 18. On the basis of Le Chatelier principle explain how temperature and pressure can be adjusted to increase the yield of ammonia in the following reaction.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$\Delta H = -92.38$ kJ mol^{-1}

What will be the effect of addition of argon to the above reaction mixture at constant volume ?

Ans. *Refer Text, Page 32–33.*

Q. 19. A sparingly soluble salt having general formula $A_x^{p+}B_y^{q-}$ and molar solubility s is in equilibrium with its saturated solution. Derive a relationship between the solubility and solubility product for such salt.

Ans. $A_x^{p+}B_y^{q-} \rightleftharpoons xA^{p+} + yB^{q-}$

If s is the solubility,

$$[A^{p+}] = xs,\ [B^{q-}] = ys$$
$$K_{sp} = [A^{p+}]^x [B^{q-}]^y = (xs)^x (ys)^y$$
$$= x^x s^x + y^y s^y = \mathbf{x^x y^y s^{x+y}}.$$

Q. 20. Write a relation between ΔG and Q and define the meaning of each term and answer the following :

(*a*) Why a reaction proceeds forward when $Q < K$ and no net reaction occurs when $Q = K$.

(*b*) Explain the effect of increase in pressure in terms of reaction quotient Q, for the reaction : $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$.

Ans. $\Delta G = \Delta G° + RT \ln Q$

ΔG = Change in free energy of the reaction

$\Delta G°$ = Standard free energy change

Q = Reaction quotient

R = Gas constant, T = Temperature (K)

(*a*) Since $\Delta G° = -RT \ln K$

$$\Delta G = -RT \ln K + RT \ln Q = RT \ln \frac{Q}{K}$$

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If Q < K, ΔG = –ve. Therefore, reaction proceeds in the forward direction.
If Q = K, ΔG = 0, Reaction is at equilibrium and no net reaction occurs.

(*b*) $K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$

If pressure is increased, then volume will decrease. Let pressure is doubled so that volume is reduced to half. The molar concentration will become double.

$$Q_c = \frac{2[CH_4]\,2[H_2O]}{2[CO]\,[2H_2]^3}$$

$$= \frac{1}{4}\frac{[CH_4][H_2O]}{[CO][H_2]^3} = \frac{1}{4}K_c$$

Thus, Q_c is less than K_c. Therefore, to re-establish the equilibrium, Q_c will tend to increase and equilibrium will shift in the forward direction.

QUICK MEMORY TEST

A. Say True or False

1. The concentrations of reactants and products become equal when equilibrium is attained.
2. A catalyst increases the speed of an equilibrium reaction and hence the amount of products formed increases.
3. The solubility of sodium hydroxide in water decreases with rise in temperature.
4. If the coefficients of a given reaction equation are doubled, then K for the new equation is also double of the original K.
5. If reaction quotient is less than K_C, the reaction will proceed in the forward direction.
6. For the reaction : $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$; $K_p = K_c$.
7. The equilibrium can be attained only when the system is closed.
8. At equilibrium rate of forward reaction becomes equal to rate of backward reaction.
9. A weak acid has a strong conjugate base and a strong acid has a weak conjugate base.
10. In the reaction : $CO_2 + OH^- \longrightarrow HCO_3^-$, CO_2 acts as a Lewis acid.
11. S^{2-} is conjugate acid of HS^-.
12. If the pK_b of a base is large, it is a strong base.
13. pH of $CuSO_4$ solution is less than 7.
14. NH_3 is not a base because it does not contain OH^- ions.
15. Precipitation occurs only when solubility product is greater than ionic product.

B. Complete the missing links

1. If the concentration quotient of a reaction is greater than its equilibrium constant, then the reaction will procced in the ..... direction.
2. Exothermic reactions are favoured by ..... in temperature.
3. The measurable properties of the system become ..... at equilibrium.
4. According to law of mass action, the rate at which a substance reacts is proportional to its .....
5. The K_p for the reaction : $CaCO_3(s) \overset{\text{heat}}{\rightleftharpoons} CaO(s) + CO_2(g)$ is .....
6. If K for the reaction : $2AB \rightleftharpoons A_2 + B_2$ is 50, then K′ for the reaction $A_2 + B_2 \rightleftharpoons 2AB$ is .....
7. The solubility of solid NH_4Cl ..... with increase in temperature.
8. On adding a catalyst to a reaction, equilibrium constant .....
9. If pressure is applied on the ice ⇌ water equilibrium, more of ..... will be formed.
10. The conjugate acid of OH^- ions is ..... and conjugate base is .....
11. pH of a $CuSO_4$ solution is ..... than 7 and that of Na_2CO_3 is ..... than 7.
12. Ionic product of water ..... with increase in temperature.
13. If K_a is ionization constant of a weak acid and K_b is the ionization constant of a weak base, then $pK_a + pK_b$ = ...
14. The solubility of AgCl in water is ..... than that in NaCl solution.
15. Precipitation occurs only when ionic product is .....than K_{sp}.

C. Choose the correct alternative

1. pH of a solution, in general *increases / decreases* with rise in temperature.
2. K_p for the reaction : $2SO_3 \rightleftharpoons 2SO_2(g) + O_2(g)$ is *less / more* than K_c.
3. The reaction : $4NO(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 5O_2(g)$ moves to *forward / backward* with increase in pressure.
4. K_c for the reaction : $I_2(s) + 5F_2(g) \rightleftharpoons 2IF_5(g)$ is *less / more* than K_p.
5. When the coefficients of a reaction equation having equilibrium constant x are doubled then the equilibrium constant for the new reaction is $x^2 / 2x$.
6. The conjugate acid of CH_3COOH is CH_3COO^- / $CH_3COOH_2^+$.
7. BCl_3 acts as a *Lewis base / Lewis acid.*
8. If the pK_a of an acid is large it is *weaker / stronger* acid.
9. The acidic strength of polyprotic acids *decreases / increases* as protons are lost.

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10. pH of CH_3COONa solution is *less/more* than 7.
11. The hydrolysis constant of a salt of strong base and weak acid is *directly/indirectly* proportional to its concentration.
12. If solubility of $PbCl_2$ is s, then its solubility product is equal to $4s^3/s^3$.
13. The conjugate acid of HCO_3^- is H_2CO_3/CO_3^{2-}.
14. If ionic product of ions is greater than K_{sp}, precipitation *will occur/will not occur*.
15. NaCl *does not/does* undergo hydrolysis.

Answers QUICK MEMORY TEST

A. Say True or False

1. **False :** The concentrations of reactants and products become constant when equilibrium is attained.
2. **False :** A catalyst increases the speed of forward as well as backward reactions to the same extent.
3. **True :** Because the dissolution is exothermic.
4. **False :** The new K is square of the original K.
5. True
6. **False :** $K_p = K_cRT$
7. True
8. True
9. True
10. True
11. **False :** Conjugate acid of HS^- is H_2S.
12. **False :** Larger the value of pK_b, weaker the base.
13. **True :** Because $CuSO_4$ is acidic being salt of strong acid and weak base.
14. **False :** NH_3 is a Lewis base.
15. **False :** Precipitation occurs only when ionic product is greater than solubility product.

B. Complete the missing links

1. backward
2. decrease in
3. constant
4. molar concentration
5. $p(CO_2)$
6. 0.02
7. increases
8. remains unchanged
9. water
10. H_2O, O^{2-}
11. less, more
12. increases
13. pK_w
14. less
15. more

C. Choose the correct alternative

1. decreases
2. more
3. forward
4. less
5. x^2
6. $CH_3COOH_2^+$
7. Lewis acid
8. weaker
9. decreases
10. more
11. indirectly
12. $4s^3$
13. H_2CO_3
14. will occur
15. does not.

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. What is the effect of halving the pressure by doubling the volume on the following reaction at 300 K ?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Ans. Since the reaction involves equal moles of reactants and products, there will be no effect on the equilibrium by changing the total pressure.

Q. 2. What effect does sodium acetate have on a solution of acetic acid according to Le-Chatelier principle ?

Solution. Acetic acid ionizes as:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

Sodium acetate ionizes as

$$CH_3COONa(aq) \rightleftharpoons CH_3COO^-(aq) + Na^+$$

Due to the presence of acetate ions furnished by strong electrolyte, CH_3COONa, the ionization of CH_3COOH will shift to the left.

Q. 3. Like water, ammonia is amphiprotic solvent. Write the equation for auto ionization of ammonia.

Solution. $2\,NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

Q. 4.Can equilibrium be achieved between water and its vapours in an open vessel ? Explain your answer and predict what happens eventually.

Ans. Equilibrium cannot be achieved between water and water vapour in an open vessel. This is because water vapour diffuse into air and their concentration above water surface is negligible. As a result, the reverse process of condensation of vapour into liquid is almost negligible. Therefore, evaporation continues till the whole water changes into vapour form. Finally, the whole water will diffuse into air as water vapour.

Q. 5. Ice melts slowly at higher altitudes. Explain why?

Ans. Ice $(s) \longrightarrow$ Water

The melting of ice is favoured at high pressure because there is decrease in volume in the forward reaction. Since at high altitudes, atmospheric pressure is low and therefore, ice melts slowly.

Q.6. Predict the effect of compression on the following equilibrium reaction :

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

Ans. The increase of pressure *i.e.* compression will favour the formation of reactants because reactants have less number of moles than products.

Q. 7. Will AgCl be more soluble in aqueous solution or NaCl solution and why ?

Ans. In NaCl solution, the Cl^- ions will increase. Since solubility product, $K_{sp} = [Ag^+]\,[Cl^-]$ remains constant. $[Ag^+]$

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will decrease. Therefore, solubility of AgCl will be less in NaCl solution than in water.

Q.8. Show that the pressure necessary to obtain 50% dessociation of PCl_5 at 500 K is numerically equal to three times the value of equilibrium constant K_p.

Ans.

	PCl_5	$\rightleftharpoons$	PCl_3 +	Cl_2
Initial moles	1		0	0
Moles at equi.	1 – 0.5 = 0.5		0.5	0.5

Total moles = 0.5 + 0.5 + 0.5 = 1.5 mol

If p is the pressure required, then

$$p(PCl_5) = \frac{0.5}{1.5} \times p = \frac{p}{3}$$

$$p(PCl_3) = \frac{0.5}{1.5} \times p = \frac{p}{3}$$

$$p(PCl_2) - \frac{0.5}{1.5} \times p = \frac{p}{3}$$

$$\therefore K_P = \frac{p(PCl_3) \times p(Cl_2)}{p(PCl_5)} = \frac{\frac{p}{3} \times \frac{p}{3}}{\frac{p}{3}} = \frac{p}{3}$$

$\therefore p = 3\ K_p$

Q.9. What is the effect of reducing volume on the following system :

$$2C(s) + O_2(g) \rightleftharpoons 2CO(g)$$

Ans. On reducing volume, pressure will increase. According to Le-Chatelier principle, equilibrium will shift to the side accompanied by decrease of pressure or decrease in number of gaseous mole i.e. backward reaction.

Q.10. At a certain temperature, the value of equilibrium constant for the reaction :

$$A_2 + 2B_2(g) \rightleftharpoons 2AB_2 \text{ is 100.}$$

What is the equilibrium constant for the reaction.

$$AB_2(g) \rightleftharpoons \frac{1}{2}A_2 + B_2 \text{ ?}$$

Ans. For the reaction,

$$A_2 + 2B_2(g) \rightleftharpoons 2AB_2,$$

equilibrium constant, $K_p = 100$

For the reverse reaction,

$$2AB_2 \rightleftharpoons A_2 + 2B_2, \quad K'_p = \frac{1}{100}$$

On dividing by 2,

$$AB_2 \rightleftharpoons \frac{1}{2}A_2 + B_2, \quad K''_p = \sqrt{\frac{1}{100}} = 0.10$$

Q.11. What will be the pH of 1M KNO_3 solution at 25°C.

Ans. KNO_3 is a salt of strong acid and strong base. Hence, its solution will be neutral. At 25°C, its pH will be 7.

Q.12. Calculate the per cent dissociation of $H_2S(g)$ if 0.1 mole of H_2S is kept in 0.4 litre vessel at 1000 K. For the reaction :

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$$

the value of K_c is 1.0×10^{-6}.

Solution.

	$2H_2S(g)$	$\rightleftharpoons$	$2H_2(g)$ +	$S_2(g)$
Initial conc.	0.1		0	0
Equiv. conc.	0.1(1–x)		0.1x	0.1x/2

Molar concentrations are :

$$[H_2S] = \frac{0.1(1-x)}{0.4}, [H_2] = \frac{0.1x}{0.4}, [S_2] = \frac{0.1x}{2 \times 0.4} = \frac{0.1x}{0.8}$$

$$K_c = \frac{[H_2]^2 [S_2]}{[H_2S]^2}$$

$$= \frac{(0.1x/0.4)^2 (0.1x/0.8)}{[0.1(1-x)/0.4]^2} = \frac{0.1x^3}{0.8(1-x)^2}$$

If x is small, $1 - x \simeq 1$

$$K_c = 1.0 \times 10^{-6} = \frac{0.1x^3}{0.8}$$

$$\therefore \quad x^3 = 8 \times 1 \times 10^{-6}$$

or $$x = 2 \times 10^{-2}$$

$$\therefore \quad \% \text{ Dissociation} = 2 \times 10^{-2} \times 100 = \mathbf{2\%}.$$

Q.13. The degree of dissociation is 0.4 at 400 K and 1.0 atm for the gaseous reaction :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Assuming ideal behaviour of all the gases, calculate the density of equilibrium mixture at 400 K and 1.0 atmosphere (Atomic mass of P = 31.0 and Cl = 35.5).

Solution.

	PCl_5	$\rightleftharpoons$	PCl_3 +	Cl_2
Initial conc.	1		0	0
Equiv. conc.	1 – 0.4 = 0.6		0.4	0.4

Total number of moles after dissociation = 0.6 + 0.4 + 0.4 = 1.4

Now, $$V = \frac{nRT}{p}$$

$$= \frac{1.4 \times 0.082 \times 400}{1} = 45.92 \text{ litre}$$

$$\text{Density} = \frac{\text{Mol.wt.}}{\text{Volume}}$$

Mol. wt. of $PCl_5 = 31 + 35.5 \times 5 = 208.5$

$$\therefore \quad \text{Density} = \frac{208.5}{45.92} = \mathbf{4.54\ g\ litre^{-1}}.$$

Q.14. 0.16 g of N_2H_4 are dissolved in water and total volume made upto 500 ml. Calculate the percentage of N_2H_4 that has reacted with water in this solution. The K_b for N_2H_4 is 4.0×10^{-16} M.

Solution. Molarity of N_2H_4 solution

$$= \frac{0.16}{32} \times \frac{1000}{500} = 0.01 \text{ M}$$

Let the amount of N_2H_4 reacted with water = α

	$N_2H_4 + H_2O$	$\rightleftharpoons$	$N_2H_5^+ + OH^-$	
Initial conc.	0.01		0	0
Equiv conc.	0.01 – α		α	α

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$$K_b = \frac{[N_2H_5^+][OH^-]}{[N_2H_4]} = \frac{\alpha \times \alpha}{0.01 - x}$$

$$4.0 \times 10^{-6} = \frac{\alpha^2}{0.01 - \alpha} = \frac{\alpha^2}{0.01} \qquad (0.01 - \alpha \approx 0.01)$$

$$\therefore \quad \alpha^2 = 4 \times 10^{-6} \times 0.01 = 4 \times 10^{-8}$$

$$\therefore \quad \alpha = 2 \times 10^{-4}$$

% of N_2H_4 reacting with water $= \frac{2 \times 10^{-4} \times 100}{0.01} =$ **2.0%.**

Q.15. The K_p value for the reaction :

$$H_2 + I_2 \rightleftharpoons 2HI$$

at 460° C is 49. If the partial pressure of H_2 and I_2 is 0.5 atm respectively, determine the partial pressure of each gas at equilibrium.

Solution.

	H_2	+	I_2	$\rightleftharpoons$	2HI
Initial pressure	0.5		0.5		0
Equi. pressure	$(0.5 - x)$		$(0.5 - x)$		$2x$

$$K_p = \frac{(pH_2)^2}{(pH_2)(pI_2)}$$

$$49 = \frac{(2x)^2}{(0.5 - x)(0.5 - x)}$$

or $$\frac{2x}{(0.5 - x)} = 7$$

or $$x = \frac{3.5}{9} = 0.389$$

$\therefore$ $pH_2 = 0.5 - 0.389 =$ **0.111 atm**

$pI_2 = 0.5 - 0.389 =$ **0.111 atm**

$pHI = 2 \times 0.389 =$ **0.788 atm.**

Q.16. Calculate the *p*H of solution obtained by mixing 150 ml of 0.2 M HCl and 150 ml of 0.1 M NaOH.

Solution. Since hydrochloric acid is 0.2 M.

Therefore, the number of gm moles of HCl in 1000 ml of the solution = 0.2

The common effect has been used to get sodium chloride of very high purity. We know learnt L

The number of gm moles of HCl in 150 ml of the solution

$$= \frac{0.2 \times 150}{1000} = \frac{30}{1000}$$

Similarly, the number of gm moles of NaOH present in 150 ml of 0.1 M solution

$$= \frac{0.1 \times 150}{1000} = \frac{15}{1000}$$

Since large number of gm moles of HCl are present in solution, $\frac{15}{1000}$ gm moles of HCl will neutralise $\frac{15}{1000}$ gm moles of NaOH on mixing the two solutions.

The number of moles of HCl left after mixing the two solutions $= \frac{30}{1000} - \frac{15}{1000} = \frac{15}{1000}$

Total volume of the solution after mixing = 150 + 150 = 300 ml

Now, 300 ml of solution contain HCl $= \frac{15}{1000}$ gm mol

$\therefore$ 1000 ml of solution contain HCl $= \frac{15}{1000} \times \frac{1}{300} \times 1000$

$= \frac{1}{20}$ gm mol per litre

or Molar concentration of H_3O^+ *i.e.*, $[H_3O^+] = \frac{1}{20}$ mol L^{-1}

$= 0.05$ mol L^{-1}

$\therefore$ pH of the solution = –log [0.05] = **1.301.**

Q.17. The solubility product of $Mg(OH)_2$ is 1.2×10^{-11}. Calculate its solubility in 0.1 M NaOH solution.

Solution. $Mg(OH)_2$ ionises as

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$

Let the solubility of $Mg(OH)_2$ in 0.1 M NaOH be x mol/litre.

According to the equation,

$[Mg^{2+}] = x, \quad [OH^-] = 2x$

Concentration of OH^- from NaOH = 0.1 M

Total conc. of OH^- in solution $= 2x + 0.1$

Now, $K_{sp} = [Mg^{2+}][OH^-]^2$

$1.2 \times 10^{-11} = (x)(2x + 0.1)^2$

Since x is very small so that $2x + 0.1 \approx 0.1$ M

$1.2 \times 10^{-11} = x \times (0.1)^2$

or $$x = \frac{1.2 \times 10^{-11}}{(0.1)^2} =$$ **1.2×10^{-9} mol L^{-1}.**

Q. 18. Given : $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$, $K_c = 6.2 \times 10^{-8}$ and K_{sp} of AgCl = 1.8×10^{-10} at 298. Calculate the concentration of the complex in 1.0 M aqueous ammonia.

Solution. For AgCl

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

$$K_{sp} = [Ag^+][Cl^-]$$

It is given that

$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$$

$$K_c = 6.2 \times 10^{-8}$$

or $$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

$$K_f = \frac{1}{K_c} = \frac{1}{6.2 \times 10^{-8}} = 1.61 \times 10^7$$

Now $$K_f = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2}$$

or $$[Ag^+] = \frac{[Ag(NH_3)_2]^+}{K_f[NH_3]^2}$$

Since the formation constant of the complex is very high, most of the Ag^+ which dissolves must be converted into complex and each Ag^+ dissolves also requires dissolution of Cl^-.

$\therefore [Ag(NH_3)]^+ = [Cl^-] = C$ (assume)

Now $$K_{sp} = [Ag^+][Cl^-]$$

$$= \frac{[Ag(NH_3)_2]^+}{K_f[NH_3]^2} \times [Cl^-]$$

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$$= \frac{C}{K_f(1)^2} \times C$$

or $C^2 = K_{sp} \cdot K_f = 1.8 \times 10^{-10} \times 1.61 \times 10^7$

$= 2.898 \times 10^{-3}$

or $C = \mathbf{5.38 \times 10^{-2}\ M.}$

Q. 19. Determine the concentration of NH_3 solution whose one litre can dissolve 0.1 mole of AgCl. K_{sp} of AgCl and K_f of $[Ag(NH_3)_2]^+$ are $1.0 \times 10^{-10}\ M^2$ and $1.6 \times 10^7\ M^{-2}$ respectively.

Solution. The reaction is

$$AgCl + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$$

$$K_{eq} = \frac{[Ag(NH_3)_2]^+[Cl^-]}{[NH_3]^2}$$

K_{sp} of $(AgCl) = [Ag^+][Cl^-]$

$$K_f = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2}$$

$K_{eq} = K_{sp} \times K_f = 1.0 \times 10^{-10} \times 1.6 \times 10^7$

$= 1.6 \times 10^{-3}$

When 0.1 mole of AgCl is dissolved in 1.0 L of solution, then at equilibrium,

$[Ag(NH_3)_2]^+ = 0.1\ M$

$[Cl^-] = 0.1\ M$

$$K_{eq} = \frac{(0.1) \times (0.1)}{[NH_3]^2}$$

$$1.0 \times 10^{-3} = \frac{1 \times 10^{-2}}{[NH_3]^2}$$

or $$[NH_3]^2 = \frac{1.0 \times 10^{-2}}{1.0 \times 10^{-3}} = 6.25\ M^2$$

or $[NH_3] = 2.5\ M$

Thus, the equilibrium concentration of NH_3 = 2.5 M. However, 0.2 mol of NH_3 are used in dissolving AgCl, so that the conc. of NH_3 is 2.5 + 0.2 = **2.7 M.**

Q. 20. The average concentration of SO_2 in atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 moles litre^{-1} and the pK_a of H_2SO_3 is 1.92, estimate the pH of acid rain on that day.

Solution. Amount of SO_2 in atmospheres = 10 ppm

$$= \frac{10}{10^6}$$

Molar conc. of SO_2 in presence of water = Amt. of SO_2 × Solubility of SO_2 in water

$= 10 \times 10^{-6} \times 1.3653\ mol\ L^{-1}$

$= 1.3653 \times 10^{-5}\ mol\ L^{-1}$

H_2SO_3 dissociates as :

	$H_2SO_3 \rightleftharpoons$	$H^+ +$	HSO_3^-
Initial conc.	1.3653×10^{-5}	0	0
Molar conc. at equiv.	$1.3653 \times 10^{-5} - x$	x	x

$$K_a = \frac{x^2}{(1.3653 \times 10^{-5} - x)}$$

Now $pK_a = 1.92$ or $-\log K_a = 1.92$

$\therefore$ $K_a = 1.2 \times 10^{-2}$

Substituting

$$1.2 \times 10^{-2} = \frac{x^2}{(1.3653 \times 10^{-5} - x)}$$

or $x^2 = 1.2 \times 10^{-2}\ (1.3653 \times 10^{-5} - x)$

Solving, we get $x = 1.364 \times 10^{-5}$

$\therefore$ $pH = -\log\ (1.364 \times 10^{-5})$

$= \mathbf{4.865}$

Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. Give one example each of a reversible and a irreversible reaction.
2. Define equilibrium constant.
3. State Le-Chatelier's principle.
4. Explain the effect of temperature on the endothermic reaction :

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

5. What is meant by dynamic nature of equilibrium?
6. State three factors which can disturb the state of equilibrium.
7. The formation of NH_3 is exothermic. What is the effect of heating the system ?
8. How is equilibrium constant related to rate constant of forward and backward reactions ?
9. State law of mass action.
10. Can a catalyst disturb the state of equilibrium ?
11. How are K_p and K_c related to each other for the reaction?

$$2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$$

12. What happens if the temperature of a saturated solution be increased ?
13. Write the expression for K_p for the reaction :

$$CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$$

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14. In which case, does the reaction go farthest to completion ?
(*i*) $K_1 = 10^{15}$ (*ii*) $K_2 = 10^3$ (*iii*) $K_3 = 10^{-5}$?
15. Can equilibrium be achieved between water and its vapours in an open vessel ? Explain.
16. What is the effect of having the pressure by doubling the volume on the following system at 775K ?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

17. Explain why pure liquids and solids are ignored while writing the equilibrium constant expression.
18. Calculate the value of K_c for the reaction :

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$K_p = 167$ at 1073 K.
19. What are amphoteric substances ? Give one example.
20. What are conjugate acid-base pairs ?
21. What is the pH of 0.1 M HCl ?
22. Calculate the concentration of SO_4^{2-} ions necessary to cause the precipitation of $BaSO_4$ ($K_{sp} = 1.5 \times 10^{-9}$) from a solution of $BaCl_2$ (0.5 M).
23. Why is ammonia termed as Lewis base ?
24. What is the concentration of H_3O^+ and OH^- ions in water at 298 K ?
25. Calculate the pH of 0.001 M HCl solution.
26. Give the conjugate acids of OH^-, HSO_4^- and NH_3.
27. State the conjugate acid-base pairs in the following:

$$CO_3^{2-} + H_2O \rightleftharpoons OH^- + HCO_3^-$$

28. Define solubility product. Write the solubility product expression for Ag_2CrO_4.
29. What do you understand by common ion effect ?
30. In the case of a salt of a weak acid and a weak base, what will be the nature of solution if $pK_a > pK_b$?
31. Why does the hydrolysis of copper sulphate solution give acidic solution ?
32. Why cannot KCl undergo hydrolysis ?
33. Define degree of hydrolysis.
34. Will the pH of an aqueous solution of NH_4Cl greater, equal or less than 7?
35. Calculate the hydrolysis constant for 0.1 M sodium acetate solution. ($K_a = 1.8 \times 10^{-5}$)

Short Answer Questions *carrying 2 or 3 marks*

1. Can equilibrium be achieved between water and its vapours in an open vessel ? Explain your answer and say what happens eventually.
2. Write the expression for equilibrium constant for the following reactions. If the concentrations are expressed in mol L^{-1}, give the units in each cas :

(*i*) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(*ii*) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(*iii*) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(*iv*) $4NH_3 + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

3. A liquid is in equilibrium with its vapour in a selected container at a fixed temperatrue. The volume of the container is suddenly increased.
(*a*) What is the initial effect of the change on vapour pressure.
(*b*) How does the rate of evporation and endensation change initially ?
(*c*) What happens when equilibrium is restored finally and what will be the final vapour pressure ?

N.C.E.R.T.

4. Define equilibrium constant. Write the equilibrium constant expression for the reaction of

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

and its reverse reaction. How are the two equilibrium constants related ?
5. How does the value of equilibrium constant predict the extent of a reaction ?
6. What will be the equilibrium constant at 717K for the reaction

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

if K for $H_2(g) + I_2(g) \rightleftharpoons 2HI$ at 717 K is 50.
7. List some important characteristics of physical equilibria.
8. Explain the effect of pressure on a system at equilibrium.
9. What will be the effect of increased pressure on the following equilibria :

(*i*) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(*ii*) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(*iii*) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(*iv*) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

10. List the conditions (no reasons) for the maximum yield of NH_3 in terms of pressure, temperature, concentration and volume.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta H = -ve$

11. Explain the effect of temperature on a system at equilibrium.
12. Using Le-Chatelier's principle, predict the effect of
(*i*) decreasing the temperature
(*ii*) increasing the temperature on each of the following :

(*a*) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -ve$

(*b*) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = +ve$

13. Explain the following with the help of Le-Chatelier's principle :
(*i*) Ice melts when pressure is applied on it.
(*ii*) Pressure has no effect on the reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; $\Delta H = -ve$

14. From the data at 298 K

(*i*) $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$; $K = 6.7 \times 10^{16}$ mol L^{-1}

(*ii*) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$; $K = 2.2 \times 10^{30}$ mol L^{-1}

(*iii*) $2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$; $K = 3.5 \times 10^{23}$ mol L^{-1}

(*iv*) $2N_2O_5(g) \rightleftharpoons 2N_2(g) + 5O_2(g)$; $K = 1.2 \times 10^{34}$ mol^5 L^{-5}

Suggest the most stable and the least oxide of nitrogen.

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15. Given that K for equation *(i)* has a value of 256 at 1000 K. Calculate the numerical values of K for other reactions *(ii)*, *(iii)* and *(iv)*.

(i) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(ii) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

(iii) $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

(iv) $SO_3 \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$

16. A liquid is in equilibrium with its vapours in a sealed container at a fixed temperature. The volume of the container is suddenly increased.

(i) What is the initial effect of the change on the vapour pressure ?

(ii) How do the rates of evaporation and condensation change initially ?

(iii) What happens when equilibrium is restored finally and what will be the final vapour pressure ?

N.C.E.R.T.

17. Phosgene dissociates as :

$COCl_2(g) \rightleftharpoons CO(g) + 2Cl(g)$

When the mixture of these gases is compressed at constant temperature, what happens to

(i) the amount of CO in the mixture

(ii) the equilibrium constant for the reaction?

18. Define the following :

(*i*) Equilibrium constant

(*ii*) Le-Chatelier principle.

19. State and explain law of mass action.

20. With the help of Le-Chatelier's principle explain

(*i*) we sweat more on a humid day

(*ii*) clothes dry quickly on a windy day.

21. What is the effect of increase in temperature and pressure on the melting of ice ?

22. How does an equilibrium constant predict the extent of the reaction ? Explain.

23. Give four characteristics of equilibrium constants.

24. Explain what is wrong with the following statements :

(*i*) The reverse reaction does not begin until all the reactants have formed.

(*ii*) If more reactant is used, the equilibrium constant will have large value.

(*iii*) If we can make a reaction go faster, we can increase the amount of product at equilibrium.

25. A system at equilibrium is described by the equation:

$$SO_2Cl_2 + \text{Heat} \rightleftharpoons SO_2 + Cl_2$$

Why does the temperature of the system increase when Cl_2 is added to the equilibrium mixture at constant volume ?

26. How will you show that equilibrium is dynamic in nature ?

27. What quantitative information can you obtain from the magntitude of equilibrium constant ?

28. Derive a relation between ionization constant and degree of ionization for acetic acid.

29. The values of ionization constants of pairs of some acids and bases are given below. Predict which is stronger in each pair :

A. *(i)* hydrofluoric acid $= 6.7 \times 10^{-4}$

(ii) oxalic acid $= 5.4 \times 10^{-2}$

B. *(i)* benzoic acid $= 6.3 \times 10^{-5}$

(ii) hydrocyanic acid $= 4.0 \times 10^{-10}$

C. *(i)* nitrous acid $= 5.1 \times 10^{-5}$

(ii) acetic acid $= 1.8 \times 10^{-5}$

D. *(i)* ammonium hydroxide $= 1.8 \times 10^{-5}$

(ii) zinc hydroxide $= 4.1 \times 10^{-5}$

30. What is ionic product of water ? What is the effect of temperature on the ionic product of water ?

31. What are conjugate acids and bases ? Select the conjugate acid-base pairs from the following reactions :

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$

32. Comment on the statement, "Even acidic solution contains OH^- ions and even a basic solution contains H^+ ions."

33. What is meant by *p*H value of a solution ? What is *p*H of neutral solution ?

34. Give the conjugate acid of

(*i*) CO_3^{2-} (*ii*) HCO_3^-

(*iii*) I^- (*iv*) HSO_4^-

(*v*) OH^- (*vi*) NH_3.

35. Give the conjugate base of

(*i*) H_2O (*ii*) HNO_3

(*iii*) HI (*iv*) NH_4^+

(*v*) HCO_3^- (*vi*) OH^-

36. Justify the statement, "All Arrhenius acids are also Bronsted acids but all Arrhenius bases are not Bronsted bases."

37. Explain the term ionic product of water. How does it vary with temperature ? What are the concentrations of H_3O^+ and OH^- ions in water at 298 K ?

38. Which of the following can act as Bronsted acid and which as Bronsted base :

H_3O^+, Cl^-, NH_3 ?

39. What do you understand by Lewis concept of acids and bases ? Justify the statement, "All Bronsted bases are also Lewis bases but all Bronsted acids are not Lewis acids".

40. Define solubility product. Write solubility product expression for the following :

(*i*) Ag_3PO_4 (*ii*) $Ag_2Cr_2O_7$

41. How does common ion effect help in the precipitation of group III hydroxides ?

42. Show that the degree of hydrolysis of a salt of weak acid and weak base is independent of concentration of the salt.

43. Explain : An aqueous solution of sodium carbonate is alkaline, copper sulphate is acidic while that of ammonium acetate is neutral.

44. Explain the following :

(*a*) A chemical equilibrium is dynamic in nature.

(*b*) In a reversible reaction, equilibrium can be achieved from either direction.

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45. (*a*) The value of equilibrium constant for the reaction:

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 48 at 270 K

What is the value of equilibrium constant for the reaction :

$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$

(*b*) Write equilibrium constant (K_c) for the reaction

$Cu^{2+}(aq) + 2Ag(s) \rightleftharpoons Cu(s) + 2Ag^{+}(aq)$

Long Answer Questions *carrying 5 marks*

1. What is chemical equilibrium ? Give its important characteristics. A chemical equilibrium is dynamic in nature. Explain.

2. State and explain Le-Chatelier-Braun principle. Discuss its applications in the manufacture of NH_3 by Haber's process.

3. What is meant by law of mass action ? Derive the expression for K_c for the general reaction : A + B = C + D.

4. Discuss the main factors which can alter the state of equilibrium in a reversible reaction.

5. What is chemical equilibrium ? Discuss its main characteristics.

6. Consider the reaction :

$\frac{1}{2}N_2 + O_2 \rightleftharpoons NO_2 + \text{Heat}$

What is the effect of the following on the equilibrium :

(*i*) decrease in temperature

(*ii*) increase in volume

(*iii*) addition of N_2

(*iv*) decrease in concentration of O_2 ?

7. Discuss Lowry-Bronsted and Lewis concepts of acids and bases.

8. What are the solubility product and common ion effect ? Discuss their applications in qualitative analysis.

9. Explain the following :

(*a*) pH of 10^{-7} M HCl is not 7.

(*b*) Degree of hydrolysis of an aqueous solution of a salt of weak acid and weak base is independent of initial concentration of the salt.

(*c*) The aqueous solution of NH_4Cl is acidic.

(*d*) A mixture of sodium acetate and acetic acid resists changes in *p*H value on adding acids or bases.

10. Define the term hydrolysis constant and the degree of hydrolysis of the salt. Derive an expression for the degree of hydrolysis, hydrolysis constant and pH of a salt of

(*i*) weak acid and strong base

(*ii*) weak base and strong base.

11. What are buffer solutions ? How do they act ? Explain the buffer action of

(*i*) an acidic buffer (*ii*) a basic buffer.

12. Write short notes on :

(*i*) Acid base indicators (*ii*) Buffer capacity

(*iii*) Common ion effect.

13. Derive an expression for

(*i*) degree of hydrolysis

(*ii*) hydrolysis constant and *p*H of a salt of weak acid and weak base.

14. What is solubility product ? How is it different from ionic product ? How can it be used to calculate the solubility of a salt like AB_2 ?

Numerical Problems *carrying 5 marks*

1. In a reaction between hydrogen and iodine at 720 K, 0.92 mol L^{-1} of hydrogen and 0.78 mol L^{-1} of iodine are found to be present in equilibrium with 6.0 mol L^{-1} of hydrogen iodide. Calculate the equilibrium constant for the reaction.

2. An equilibrium mixture

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

contained in a 1 L flask at 600°C was found to contain 0.5 mol of SO_2, 0.12 mol of O_2 and 5.0 mol of SO_3. Calculate K_p and K_c at 600°C.

3. When 20 g of $CaCO_3$ were heated to 800°C in a 10 L flask, 30% of $CaCO_3$ remained unreacted at equilibrium. Calculate K_p for the decomposition of $CaCO_3$.

4. K_c for the reaction ;

$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$

is 1×10^{-6} at 100 K.

What is the % dissociation of H_2S if 1 mole of H_2S is introduced in a 1.1 L of flask at 1000 K ?

5. When PCl_5 is heated, it gasifies and dissociates into PCl_3 and Cl_2. The density of gas mixture at 200°C is 70.2. Find the percentage dissociation of PCl_5.

6. When 20g of $CaCO_3$ were put into 10 L flask and heated at 1073 K, 35% $CaCO_3$ remained unreacted at equilibrium. Calculate K_p for decomposition of $CaCO_3$ at 1073 K.

7. The equilibrium constant K_p for the reaction at 800 K:

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

is 900 atm^{-1}. A mixture containing SO_3 and O_2 having partial pressure of 1 and 2 atm respectively is heated at constant volume to equilibrium. Calculate the partial pressure of each gas at 800 K.

8. The molar solubility of lead iodate, $Pb(IO_3)_2$ is 4.0×10^{-5} mol/L at 25°C. Calculate its K_{sp}.

9. When 0.01 M HCl solution is added to 0.01 M $Pb(NO_3)_2$ solution, will a precipitate of $PbCl_2$ be formed or not? $K_{sp} = 1.6 \times 10^{-5}$.[**Ans.** Ionic product = 1.0×10^{-6}, precipitation will not occur]

10. How many grams of sodium hydroxide must be dissolved in one litre of solution to give it a *p*H of 12 ?

11. $\frac{1}{2}$ litre of 2×10^{-3} M $AlCl_3$ and $\frac{1}{2}$ litre of 4×10^{-2} M solution of NaOH are mixed and the solution is diluted to 10^2 litres with water at room temperature. Will a precipitate form ? Given K_{sp} $Al(OH)_3 = 5 \times 10^{-33}$.

12. The solubility product of PbI_2 at 30°C is 1.4×10^{-8}. Calculate the solubility of the salt in 0.1 M KI solution at this temperature.

13. The dissociation constants of ammonia and acetic acid being equal what would be the *p*H of ammonia solution if that of an acetic acid solution of equal strength is 3.2. Given K_w for water = 10^{-14}.

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14. The self ionisation constant of pure formic acid, $K = [HCOOH_2]^+ [HCOO^-]$ has been estimated as 10^{-6} at room temperature. What percentage of formic acid molecules in pure formic acid are converted to formate ion ? The density of formic acid is 1.22 g/cm^3.

15. Calculate the pH of solution obtained by mixing 10 mL of 0.1 M HCl and 40 ml of 0.2 M H_2SO_4.

16. K_{sp} of $PbCl_2$ is 10^{-13}. What will be the concentration of Pb^{2+} in a solution prepared by mixing 100 ml of 0.1 M $Pb(NO_3)_2$ and 1 ml of 1M HCl ?

17. Calculate the pH of 0.05 M aqueous NaCN solution. pK_b of CN^- = 4.70

18. The concentration of sulphide ion in 0.1 M HCl solution saturated with H_2S is 1.0×10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following :

$FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$.

In which solutions precipitation will occur.

K_{sp} values are : FeS : 6.3×10^{-18}, MnS = 2.5×10^{-3}, ZnS = 1.6×10^{-24}, CdS = 8.0×10^{-27}

19. What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volume, there is no precipitation of iron sulphide? ($K_{sp} = 6.3 \times 10^{-18}$)

Hints & Answers for Revision Exercises

Very Short Answer Questions

1. Increase of temperature favours forward reaction.

7. Heating the system will not favour the formation of NH_3.

8. $K = \dfrac{K_f}{K_b}$

11. $K_p = K_c (RT)^{-1}$

13. $K_p = p_{co_2}$

14. (*iii*)

19. Water

21. 1

22. $[SO_4^{2-}] = \dfrac{1.5 \times 10^{-9}}{0.5}$

$= 3.0 \times 10^{-10}$ M, greater than 3×10^{-10} M

24. $[H_3O^+] = [OH^-] = 1 \times 10^{-7}$ mol L^{-1}

25. 3

26. H_2O, H_2SO_4, NH_4^+

27. CO_3^{2-}, HCO_3^-, H_2O, OH^-

28. $K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$

30. alkaline

34. less than 7

35. 5.56×10^{-10}

Short Answer Questions

2. Units (*i*) mol L^{-1} (*ii*) mol^{-2} L^2 (*iii*) no units (*iv*) mol L^{-1}.

4. $K = \dfrac{[HI]}{[H_2][I_2]}$ and $K' = \dfrac{[H_2][I_2]}{[HI]^2}$ K; $\dfrac{1}{K'}$

6. 2×10^{-2}

9. With increase in pressure (*i*) increases (*ii*) decreases (*iii*) increases (*iv*) no change

14. Stable NO_2, least stable N_2O_3

15. 1/256, 16, 1/16

29. A–(*ii*), B–(*i*), C–(*i*), D–(*ii*).

31. NH_3, NH_4^+; H_3O^+, OH^-; HCN, CN^-; H_2O, H_3O^+

33. 7

34. (*i*) HCO_3^- (*ii*) H_2CO_3 (*iii*) HI (*iv*) H_2SO_4 (*v*) H_2O (*vi*) NH_4^+

35. (*i*) OH^- (*ii*) NO_3^- (*iii*) I^- (*iv*) NH_3 (*v*) CO_3^{2-} (*vi*) O_2^-

40. (*i*) $[Ag^+]^3 [PO_4^{3-}]$ (*ii*) $[Ag^+]^2 [Cr_2O_7]^{2-}$

45. (*a*) 6.83 (*b*) $K_c = \dfrac{[Ag^+(aq)]^2}{[Cu^{2+}(aq)]}$

Numerical Problems

1. The reaction is

$$H_2 + I_2 \rightleftharpoons 2HI$$

Equi conc. 0.92 0.78 6.0

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{(6.0)^2}{(0.92)\times(0.78)} = \mathbf{50.17}$$

2. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Equi. conc. 0.5 0.12 5.0

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(5.0)^2}{(0.5)^2(0.12)} = \mathbf{833.3\ mol^{-1}\ L.}$$

$K_p = K_c (RT)^{\Delta n}$

$K_p = 833.3 \times (0.082 \times 873)^{-1} = \mathbf{11.64\ atm^{-1}.}$

3. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Initial. conc. of $CaCO_3 = \dfrac{20}{100} = 0.2$

Moles of $CaCO_3$ after dissociation $= 0.2 \times \dfrac{70}{100}$

$= 1.4$ mol.

Moles of CO_2 formed $= 1.4$ mol

$$[CO_2] = \frac{1.4}{10} = 0.14 \text{ M}$$

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Applying $pV = nRT$

$$p_{CO_2} = \frac{0.14 \times 0.0821 \times 1073}{10} = \mathbf{1.23\ atm.}$$

$$K_p = p_{CO_2} = \mathbf{1.23\ atm}$$

4. Molar conc. of $H_2S = \frac{1}{1.1} = 0.909\ mol\ L^{-1}$

	$2H_2S$	$\rightleftharpoons$	$2H_2$	+	S_2
Initial conc.	0.909		0		0
At equiv.	0.909 (1 –α)		0.909 α		0.909 α/2

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{(0.909\alpha)^2(0.909\alpha/2)}{[(0.909)(1-\alpha)]^2}$$

$$1 \times 10^{-6} = \frac{0.909\,\alpha^3}{2(1-\alpha)^2}$$

Now, $1 - \alpha \approx 1$

$$\therefore \quad 1 \times 10^{-6} = \frac{0.909\,\alpha^3}{2} \text{ or } \alpha = 1.30 \times 10^{-2}$$

% dissociation = **1.30 %**

5.

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Initial conc.	1		0		0
At equiv.	1– α		α		α

Total moles = $1 - \alpha + \alpha + \alpha = 1 + \alpha$

Volume occupied by 1 mole of $PCl_5(g) = \frac{1}{V}$ litre

Volume occupied by $(1 + \alpha)$ mole of gases at equiv. $= \frac{1+\alpha}{V}$ litre

Now, density $D = \frac{1}{V}$

Density before dissciation, $D = \frac{1}{V}$

Density after dissociation, $d = \frac{1}{(1-\alpha)V}$

$$\frac{D}{d} = 1 + \alpha$$

or $$\alpha = \frac{D}{d} - 1 \text{ or } = \frac{D-d}{d}$$

Vap. density D of $PCl_5 = \frac{31 + 177.5}{2} = 104.25$

Observed density = 70.2

$$\therefore \quad \alpha = \frac{104.25 - 70.2}{70.2} = 0.485$$

or $\alpha = 48.5\%$

6. Moles of $CaCO_3$ intially present $= \frac{20}{100} = 0.20$

Moles of $CaCO_3$ left at equilibrium $= \frac{0.20 \times 35}{100} = 0.07$

Moles of $CaCO_3$ reacted = 0.20 – 0.07 = 0.13

	$CaCO_3(s)$	$\rightleftharpoons$	$CaO(s)$	+	$CO_2(g)$
Initial conc.	0.20		0		0
At equiv.	0.07		0.13		0.13

Pressure of CO_2, $p = \frac{n\,RT}{V}$

$$= \frac{0.13 \times 0.0821 \times 1073}{10} = 1.145$$

$$K_p = p(CO_2) = \mathbf{1.145\ atm}$$

7.

	$2SO_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2SO_3(g)$
Initial conc.	0		2		1
At equiv.	2x		2 + x		1 – 2x

$$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2(p_{O_2})} = \frac{(1-2x)^2}{(2x)^2(2+x)} = 900\ atm^{-1}$$

Assuming x to be very small

$$\frac{1}{(4x^2) \times 2} = 900\ atm^{-1}$$

Solving $x = 0.118$ atm

$\therefore$ $p(SO_2) = 2 \times 0.0118 = 0.0236$ atm,

$p(O_2) = 2 + 0.0118 = 2.0118$ atm

$p(SO_3) = 1 - 2 \times 0.0118 = 0.976$ atm.

8. $K_{sp} = [Pb^{2+}]\,[IO_3^-]^2$

The molar solubility of $Pb(IO_3)_2$ is $4.0 \times 10^{-5}\ mol\ L^{-1}$

$\therefore$ $[Pb^{2+}] = 4.0 \times 10^{-5}\ mol\ L^{-1}$,

$[IO_3^-] = 2 \times 4.0 \times 10^{-5}\ mol\ L^{-1}$

$\therefore$ $K_{sp} = (4.0 \times 10^{-5})(8.0 \times 10^{-5})^2$

$= \mathbf{2.56 \times 10^{-13}}$

9. K_{sp} for $PbCl_2 = [Pb^{2+}]\,[Cl^-]^2$

$[Pb^{2+}] = [Pb(NO_3)_2] = 0.01$ M,

$[Cl^-] = [HCl] = 0.01$ M

$\therefore$ Ionic produt $= [Pb^{2+}]\,[Cl^-]^2$

$= (0.01) \times (0.01)^2 = 1.0 \times 10^{-6}$

Since ionic product is less than K_{sp} (1.6×10^{-5}), **no precipitate will be formed.**

10. $-\log [H_3O] = 12$ or $[H_3O^+] = 1 \times 10^{-12}$

$$[OH^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-12}} = 1 \times 10^{-2} = 0.01\ mol\ L^{-1}$$

$\therefore$ Amount of NaOH = $0.01 \times 40 = \mathbf{0.4\ g\ L^{-1}}$.

11. The solubility equilibrium of $Al(OH)_3$ is

$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$

On mixing $\frac{1}{2}$ litre of $AlCl_3$ and $\frac{1}{2}$ litre of NaOH, the total solution is made 10^2 litres by adding water.

Concentration of $AlCl_3$

$$= \frac{2 \times 10^{-3}}{10^2} \times \frac{1}{2} = 1 \times 10^{-5}\ M$$

Concentration of NaOH

$$= \frac{4 \times 10^{-2}}{10^2} \times \frac{1}{2} = 2 \times 10^{-4}\ M$$

Since $AlCl_3$ ionises as :

$AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^-$

$[Al^{3+}] = [AlCl_3] = 1 \times 10^{-5}\ M$

Since NaOH ionises as :

$NaOH \rightleftharpoons Na^+ + OH^-$

$[OH^-] = [NaOH] = 2 \times 10^{-4}$

Now, ionic product = $[Al^{3+}]\,[OH^-]^3$

$= 1 \times 10^{-5} \times (2 \times 10^{-4})^3 = 8 \times 10^{-17}$

As the product of concentration of ions of the salt is more than K_{sp}, the salt will be precipitated.

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12. $KI \rightleftharpoons K^+ + I^-$

$[I^-] = [KI] = 0.1\ M$

When PbI_2 is dissolved in KI (0.1M) solution, then KI will give 0.1 M I^- ions. Let the solubility of PbI_2 be x mol/litre.

$$PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$$

$$[Pb^{2+}] = x, [I^-] = 2x + 0.1$$

$$K_{sp} = [Pb^{2+}][I^-]^2$$

$$1.4 \times 10^{-8} = (x)(2x + 0.1)^2$$

Since PbI_2 is a weak electrolyte, $2x$ may be neglected in comparison to 0.1.

$$1.4 \times 10^{-8} = x(0.1)^2$$

or $$x = \frac{1.4 \times 10^{-8}}{(0.1)^2} = \mathbf{1.4 \times 10^{-6}\ M.}$$

13. $K_b(NH_4OH) = K(CH_3COOH)$

For equal strengths : $\sqrt{cK_b} = \sqrt{cK_a}$

$$[OH^-]_{(NH_4OH)} = [H_3O^+]_{(CH_3COOH)}$$

$$-\log[OH^-]_{NH_4OH} = -\log[H_3O^+]_{CH_3COOH}$$

$$pOH\ (NH_4OH) = pH\ (CH_3COOH)$$

$$pOH\ (NH_4OH) = 3.2$$

$$pH\ (NH_4OH) = 14 - 3.2 = \mathbf{10.8.}$$

14. Wt. of formic acid in 1L solution

$$= 1.22 \times 1000 = 1.22 \times 10^3\ g$$

$$[HCOOH] = \frac{1.22 \times 10^3}{46} = 26.5\ M$$

Since in case of auto ionisation,

$$[HCOOH_2^+] = [HCOO^-]$$

$$[HCOOH_2^+][HCOO^-] = 10^{-6}$$

$$\therefore\ [HCOO^-] = 10^{-3}$$

$$\therefore\ \%\ \text{Dissociation of HCOOH} = \frac{[HCOO^-]}{[HCOOH]} \times 100$$

$$= \frac{10^{-3}}{26.5} \times 100 = \mathbf{0.004\ \%}$$

15. Amount of H^+ in 10 ml of 0.1M HCl $= \frac{0.1}{1000} \times 10 = 0.001$

Amount of H^+ in 40 ml of 0.2M H_2SO_4

$$= \frac{2 \times 0.2}{1000} \times 40 = 0.016$$

Total $H^+ = 0.001 + 0.016 = 0.017$

Vol. of solution obtained = 10 + 40 = 50 ml

$$\therefore\ \text{Molarity of } H^+ = \frac{0.017}{50} \times 1000 = 0.34\ M$$

$$pH = -\log(0.34) = \mathbf{0.468}$$

16. $Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2 + 2HNO_3$

Millimoles added			
$100 \times 0.1 = 10$	$1 \times 1 = 1$	0	0
Millimoles left			
9.5	0	0.5	1

Total $[Pb^{2+}]$ in solution $= \frac{9.5 + 0.5}{101}$

Now, if $PbCl_2$ is precipitated, then contribution of 0.5 of $[Pb^{2+}]$ from $PbCl_2$ be left

For precipitation,

Ionic product $> K_{sp}$

Ionic product $= [Pb^{2+}][Cl^-]^2$

$$= \left(\frac{10}{101}\right)\left(\frac{1}{101}\right)^2 = 9.70 \times 10^{-6}$$

The ionic product is greater than K_{sp}, so that precipitation will occur

$$[Pb^{2+}] = \frac{9.5}{101} = 9.4 \times 10^{-2}\ mol\ L^{-1}$$

17. $CN^- + H_2O \rightleftharpoons OH^- + HCN$

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} = \frac{[OH^-]^2}{[CN^-]}$$

$$\therefore\ pK_b = -\log K_b = -2\log[OH^-] + \log[CN^-]$$

$$[CN^-] = [NaCN]$$

$$4.70 = -2\log[OH^+] + \log(0.5)$$

$$2\log[OH^-] = -4.70 - 0.30$$

or $$2\log[OH^-] = -5.00$$

$$-\log[OH^-] = 2.50$$

$$pOH = 2.50$$

$$\therefore\ pH = 14 - 2.5 = \mathbf{11.5}$$

18. Precipitation will occur in the solution in which ionic product is greater than solubility product, K_{sp}.

10 mL of solution containing S^{2-} ions is mixed with 5 mL of metal salt solution so that total volume becomes 15 mL.

$$[S^{2-}] = 1.0 \times 10^{-19} \times \frac{10}{15} = 6.67 \times 10^{-20}$$

$$[Fe^{2+}] = [Mn^{2+}] = [Zn^{2+}] = [Cd^{2+}]$$

$$= \frac{5}{15} \times 0.04 = 1.33 \times 10^{-2}\ M$$

Ionic product for each of these will be

$$= [M^{2+}][S^{2-}]$$

$$= (1.33 \times 10^{-2}) \times (6.67 \times 10^{-20})$$

$$= 8.87 \times 10^{-22}$$

Since ionic product is greater than the K_{sp} of ZnS and CdS, therefore, $ZnCl_2$ and $CdCl_2$ solution will form precipitates.

19. Suppose the concentration of each of $FeSO_4$ and Na_2S be x mol L^{-1}. Then after mixing equal volumes,

$$[FeSO_4] = [Na_2S] = \frac{x}{2}\ mol\ L^{-1}$$

or $$[Fe^{2+}] = [S^{2-}] = \frac{x}{2}\ M$$

$$K_{sp}\ \text{of FeS} = [Fe^{2+}][S^{2-}]$$

$$6.3 \times 10^{-8} = \frac{x}{2} \times \frac{x}{2}$$

$$\therefore\ x = \mathbf{5.02 \times 10^{-9}\ M}$$

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Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

❑ SIMULTANEOUS EQUILIBRIUM

A simultaneous equilibrium occurs when more than one equilibrium exists simultaneously in the same container. In such cases, the same species may be involved in more than one equilibrium and its concentration at equilibrium is the same in all those equilibria under the same thermodynamic conditions. For example, in the following two equilibria, the species C(*g*) occurs in both the equilibria and therefore its concentration at equilibrium will be same.

$$A(s) \rightleftharpoons B(g) + C(g)$$

$$D(s) \rightleftharpoons E(g) + C(g)$$

For example,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

In this system, CO_2 (*g*) is the common species in these two equilibria and hence its concentration will be the same for both finally.

This concept may be illustrated by the following examples.

Example 1. At a certain temperature, dissociation constant, K_p for decomposition of calcium carbonate

$$\mathbf{Ca\,CO_3(s) \rightleftharpoons CaO(s) + CO_2(g)}$$

is 5.2×10^{-2} atm and for the second reaction,

$$\mathbf{C(s) + CO_2(g) \rightleftharpoons 2CO(g)}$$

is 2.4 atm respectively. Calculate the partial pressure of CO at this temperature when solid carbon, CaO and $CaCO_3$ are mixed and allowed to attain equilibrium.

Solution. For the reaction,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K_p = p_{CO_2} = 5.2 \times 10^{-2} \text{ atm}$$

The concentration of CO_2 will be same in both equilibria. In the reaction,

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

$$K_p = \frac{(p_{CO})^2}{p_{(CO_2)}} = 2.4 \text{ atm}$$

or $$p(CO)^2 = p_{(CO_2)} \times 2.4$$

$$= 5.2 \times 10^{-2} \times 2.4$$

$$= 12.48 \times 10^{-2}$$

or $$p(CO) = \sqrt{12.48 \times 10^{-2}}$$

$$= 0.353 \text{ atm}$$

Example 2. When N_2O_5 is heated at a certain temperature, it dissociates as:

$$\mathbf{N_2O_5(g) \rightleftharpoons N_2O_3(g) + O_2(g)}$$ **and K_C is 2.5**

At the same time N_2O_3 also decomposes as

$$\mathbf{N_2O_3(g) \rightleftharpoons N_2O(g) + O_2(g)}$$

If initially 4.0 mol of N_2O_5 are taken in 1.0 L flask and allowed to attain equilibrium, the concentration of O_2 was found to be 2.5 mol L^{-1}. Calculate the equilibrium concentration of N_2O.

Solution. Let x mol of N_2O_5 dissociates giving x mol of N_2O_3 and x mol of O_2. Further let y mol of N_2O_3 decompose to give y mol of N_2O and y mol of O_2. Then, $x - y$ mol of N_2O_3 will be present at equilibrium.

	N_2O_5	$\rightleftharpoons$	N_2O_3	+	O_2	...(*i*)
Initial	4		0		0	
At. equi.	(4–x)		x–y		x	

	N_2O_3	$\rightleftharpoons$	N_2O	+	O_2	...(*ii*)
	y		y		y	

Moles of O_2 formed = $x + y = 2.5$ ...(*iii*)

From eqn. (*i*)

$$K_C = \frac{[N_2O_3][O_2]}{[N_2O_5]} = 2.5$$

or $$\frac{(x-y)(x+y)}{4-x} = 2.5$$

$$\frac{(x-y) \times 2.5}{4-x} = 2.5$$

or $$x - y = 4 - x$$

or $$2x - y = 4 \quad ...(iv)$$

Solving eqn. (*iii*) and eqn. (*iv*)

$$2x - y = 4$$

Adding $$x + y = 2.5$$

$$3x = 6.5$$

or $$x = \frac{6.5}{3} = 2.166 \text{ mol}$$

$$y = 2.5 - 2.166 = 0.334$$

∴ Equilibrium conc. of N_2O = 0.334 mol L^{-1}

❑ CALCULATION OF DEGREE OF DISSOCIATION FROM VAPOUR DENSITY MEASUREMENTS

The degree of dissociation in a reversible reaction may be calculated with the help of vapour density of the equilibrium mixture. It can be calculated for those substances which are accompanied by change in number of moles.

Let us consider a general reaction

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$$AB(g) \rightleftharpoons A(g) + B(g)$$

Suppose we have 1 mol of AB and α is the degree of dissociation at the experimental temperature.

	$AB(g)$		$A(g)$	+	$B(g)$
No. of moles before dissociation	1		0		0
No. of moles after dissociation	1–α		α		α

Suppose the volume occupied by the vapour per mole = V litre, then

Before dissociation total no. of moles = 1, total volume = V litres.

If D is the vapour density before dissociation (called theoretical vapour density), then

$$D \propto \frac{1}{V} \qquad ...(i)$$

$$\left(\therefore \text{Density} \propto \frac{1}{\text{Volume}}\right)$$

Total no. of moles after dissociation

$$= 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

Total volume occupied by reaction mixture

$$= (1 + \alpha)\ V \text{ litres}$$

If d is the density of vapour at equilibrium (called observed density), then

$$d \propto \frac{1}{(1+\alpha)V} \qquad ...(ii)$$

Dividing eqn. (i) by eqn. (ii)

$$\frac{D}{d} = \frac{1/V}{1/(1+\alpha)V} = 1 + \alpha$$

or $$\alpha = \frac{D}{d} - 1$$

or $$\alpha = \frac{D - d}{d}$$

If 1 mole of a substance dissociates in n moles of substances, then above equation may be written as:

$$A \rightarrow nB$$

$$\alpha = \frac{D - d}{(n-1)d}$$

For example, for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$\alpha = \frac{D - d}{(2-1)d} = \frac{D - d}{d}$$

In terms of molecular mass

Molecular mass = 2 Vapour Density. Therefore, above equation becomes

$$\alpha = \frac{M_t - M_o}{M_o}$$

where M_t is theoretical (or calculated) molecular mass and M_o is observed molecular mass.

The observed molecular mass can also be calculated from the mass of a definite volume of the vapour at a particular temperature, using the relation,

$$pV = nRT$$

or $$pV = \frac{wRT}{M} \quad \text{or} \quad M_o = \frac{wRT}{pV}$$

Illustrations

Example 1. *At a constant temperature, vapour density of N_2O_4 is found to be 32. Calculate percent degree of dissociation of N_2O_4.*

Solution: Molecular mass of N_2O_4

$$= 2 \times 14 + 4 \times 16 = 92$$

$$\text{Vapour density} = \frac{\text{Molecular mass}}{2} = \frac{92}{2} = 46$$

or $D = 46$

Observed density, d=32

Degree of dissociation,

$$\alpha = \frac{D - d}{d}$$

$$= \frac{46 - 32}{32} = 0.4375 \text{ or } 43.75\%$$

Example 2. *The vapour density of PCl_5 at 500 K is found to be 68.4. Calculate the degree of dissociation of PCl_5 at 500 K.*

Solution. Molecular mass of $PCl_5 = 31 + 5 \times 35.5$

$$= 208.5$$

Theoretical density,

$$D = \frac{208.5}{2} = 104.25$$

Observed vapour density, $d = 68.4$

∴ Degree of dissociation,

$$\alpha = \frac{D - d}{d} = \frac{104.25 - 68.4}{68.4} = 0.524$$

or $= \mathbf{52.4\%}$

❑ CALCULATION OF DEGREE OF DISSOCIATION FROM PRESSURE AND TEMPERATURE MEASUREMENTS

Let a reversible reaction is carried out in a closed vessel of volume V at temperature T_1 and pressure p_1. After attainment of equilibrium at temperature T_2, pressure of the reaction mixture be p_2. If we start with a moles of AB and α is the degree of dissociation, then

	AB		$A(g)$	+	$B(g)$
Initial moles	a		0		0
At equiv.	$a(1-\alpha)$	=	$a\alpha$		$a\alpha$

Total moles at equilibrium $= a(1-\alpha) + a\alpha + a\alpha$

$$= a(1+\alpha)$$

Applying gas equation,

$$pV = nRT$$

For initial conditions,

$$p_1V = aRT_1 \qquad ...(i)$$

For equilibrium conditions

$$p_2V = a\,(1+\alpha)\,RT_2 \qquad ...(ii)$$

Dividing eqn. (i) by eqn. (ii)

$$\frac{p_1}{p_2} = \frac{a}{a(1+\alpha)}\frac{T_1}{T_2} = \frac{T_1}{(1+\alpha)T_2}$$

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or $(1+\alpha) = \frac{T_1}{T_2} \times \frac{p_2}{p_1}$ or $\alpha = \frac{T_1 p_2}{T_2 p_1} - 1$

If temperature is constant *i.e.* $T_2 = T_1$

$$\alpha = \frac{p_2}{p_1} - 1 = \frac{p_2 - p_1}{p_1}$$

Example 3. At 573K, 1L of partially dissociated PCl_5 at 1 atm. pressure weighs 2.486 g. Calculate the percentage dissociation of PCl_5 at this temperature.

Solution. Applying

$$pV = nRT$$

or $$pV = \frac{wRT}{M}$$

or $$M_o = \frac{wRT}{pV} = \frac{2.486 \times 0.082 \times 573}{1 \times 1}$$

$$= 116.8$$

$$M_t(PCl_5) = 31 + 5 \times 35.5 = 208.5$$

$$\therefore \quad \alpha = \frac{M_t - M_o}{M_o}$$

$$= \frac{208.5 - 116.8}{116.8} = 0.785$$

Degree of dissociation,

$$\alpha = 78.5\%$$

❑ ACID BASE TITRATIONS

Theory of Titrimetry

Volumetric method is one of the most useful methods for quantitative analysis which involves accurate measurement of the volumes of solutions undergoing a chemical change. In this method, a standard solution of the reagent is taken in a measuring vessel known as *burette* and is then gradually added to the solution to be analysed (in a *titration flask*). The process is continued until it is found by a suitable method that the amount of reagent which has been added is equivalent to the substance being determined. This operation is called *titration* and, therefore, volumetric analysis is also called **titrimetric analysis** or **titrimetry**.

Therefore, one of the solutions is taken in a burette and the second is taken in the titration flask. The exact point at which a chemical reaction is completed during the titration is called the **end point** or **equivalent point**. In order to determine the completion of the reaction (or end point) a substance is used known as **indicator**. This shows change in colour just at the stage when the reaction is complete.

Theory of indicators

Indicators are *the substances which indicate by change in colour the completion (or end point) of a chemical reaction*.

The indicators used in acid base neutralisation titrations are complex compounds which are weak acids or weak bases. These have different colours in the ionized and unionized forms. These show different colour changes in a definite pH range.

$$\underset{\text{Acid form (One colour)}}{HIn\,(aq)} \rightleftharpoons H^+(aq) + \underset{\text{Base form (Different colour)}}{In^-(aq)}$$

For example, phenolphthalein is a weak organic acid which ionizes as:

$$\underset{\text{Colourless}}{HPh\,(aq)} \rightleftharpoons H^+(aq) + \underset{\text{Pink}}{Ph^-(aq)}$$

As the medium changes from acidic to basic, or vice versa, the equilibrium shifts either towards right or towards left and so the colour changes. For example, in acidic medium (*i.e.* in the presence of excess H^+ ions), the equilibrium shifts towards left (Le-Chatelier principle). This results in the formation of colourless unionized HPh molecules. Hence, acidic solution of phenolphthalein will be colourless.

$$HPh \rightleftharpoons Ph^- + H^+$$

$$HCl \rightleftharpoons H^+ + Cl^-$$

(Due to excess of H^+ ions on the right, the equilibrium shifts towards left).

In the basic medium, OH^- ions from the base react with H^+ ions to form unionized H_2O molecules. As a result, the equilibrium shifts towards right and therefore, the concentration of pink coloured Ph^- ions increases. Hence basic solution will be pink.

$$\underset{\text{Pink}}{HPh} \rightleftharpoons Ph^- + H^+ \quad ...(i)$$

$$\underset{\text{from base}}{H^+ + OH^-} \rightleftharpoons H_2O$$

(Due to decrease in H^+ on the right, equilibrium shifts towards right.)

This theory also explains as to why weak base like NH_4OH cannot be titrated with a strong acid like HCl. A weak base, like, NH_4OH ionises to a very small extent:

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

The less number of OH^- ions produced are not sufficient to shift the equilibrium of reaction (*i*) towards right to produce a large number of coloured Ph^- ions.

Hence pink colour does not appear until a large excess of weak base is added to get visible colour change *i.e.* end point.

Similarly, methyl orange is a weak organic base. Its ionized form is red while its unionized form is yellow.

$$\underset{\substack{\text{Methyl orange}\\\text{(yellow)}}}{MeOH} \rightleftharpoons \underset{\text{(Red)}}{Me^+} + \underset{\text{(Colourless)}}{OH^-}$$

Now, the addition of a base like NaOH will give OH^- ions. This increases the concentration of OH^- ions and therefore, shifts the equilibrium in the backward direction (Le-Chatelier's principle). As a result, the colour or the solution becomes yellow. Therefore, in basic solution, methyl orange gives yellow colour.

$$\underset{\text{(Yellow)}}{MeOH} \rightleftharpoons \underset{\text{(Red)}}{Me^+} + OH^- \quad ...(i)$$

$$NaOH \rightleftharpoons Na^+ + OH^-$$

(Due to increase of OH^- on the right side equilibrium (*ii*) shifts to the left.)

On the other hand, in the presence of an acid, like HCl, the H^+ ions formed combine with OH^- ions of the indicator to form feebly ionised water molecules. Therefore, the equilibrium shifts towards right and in acidic solutions, methyl orange gives red colour.

$$\underset{\text{(Yellow)}}{MeOH} \rightleftharpoons \underset{\text{(Red)}}{Me^+} + OH^- \quad ...(ii)$$

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$$H^+ + OH^- \rightleftharpoons H_2O$$

(Due to decrease in OH^- ions, equilibrium shifts towards the right).

This theory could explain as to why methyl orange cannot be used as an indicator in neutralisation reaction involving a weak acid like acetic acid, CH_3COOH. This is because, weak acid ionises to a small extent as:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

The small number of H^+ ions will not be sufficient to shift the equilibrium of equation (*ii*) to the forward direction unless the acid added is in excess. Therefore, the end point will not be sharp.

Acid-Base Titrations and pH at the End point

During the acid base titration, the concentration of H^+ or OH^- ions change and therefore pH also changes. In acid-base titrations, successive amounts of a base are added to a definite amount of an acid (or vice versa) and the pH of the solution is noted after every addition. **The plot of pH against the amount of alkali added** is called a **titration curve**. The shape of the curve depends upon the ionization constants of the acid and base used in the titration. The point at which there is a sudden jump in pH (point of inflection) when a small amount of titrant is added is called **equivalence point**.

Neutralisation of a strong acid by a strong base

To understand how pH changes during acid base titrations, let us consider the titration of 50 mL of 0.1 N HCl against 0.1 N NaOH solution. The pH at different additions of NaOH may be theoretically calculated.

Initially, the solution in the flask is 0.1 N HCl and therefore,

$$[H^+] = 0.1 \quad \text{or} \quad 1 \times 10^{-1},\ pH = 1.0$$

When 10 mL of 0.1 N NaOH has been added, it will neutralise 10 mL of 0.1 N HCl so that

HCl left in solution = 40 mL,

Total volume of solution = 50 + 10 = 60 mL

To calculate normality of resulting solution,

$$N_1 V_1 \equiv N_2 V_2$$

$$0.1 \times 40 = N_2 \times 60 \text{ or } N_2 = \frac{0.1 \times 40}{60} = 0.0667 \text{ M}$$

$$[H^+] = 0.0667 \text{ M}$$

$$pH = 1.18$$

Similarly, when 20, 30 or 40 mL of NaOH solution have been added, the corresponding pH values can be calculated as given in Table 1.

Table 1. Titration of 50.0 mL of 0.1 N HCl with 0.1 N NaOH solution

Volume of 0.1 NaOH added	$[H^+]$ mol/L	pH
0.0	0.1	1
10.0	0.667	1.18
20.0	0.0429	1.37
30.0	0.025	1.60
40.0	0.0111	1.95
49.0	0.0010	3.0
50.0	1×10^{-7}	7.0
50.1	1×10^{-10}	10.0
51.0	1.01×10^{-11}	11.0
60.0	1.1×10^{-12}	11.96
70.0	0.599×10^{-12}	12.22

Up to the addition of 49.9 mL of 0.1 N NaOH, the normality of HCl or $[H^+]$ can be calculated from the following relation.

$$\text{Normality of HCl or } [H^+] = \left(\frac{50 - v}{50 - v}\right) \times 0.1$$

where v is the volume of 0.1 N NaOH added

When 50 mL of 0.1 N NaOH has been added, the end point of the titration is reached and all the acid is neutralised. The solution contains only NaCl and $[H^+] = 10^{-7}$ M or pH = 7.0

Further addition of even a very small amount of 0.1N NaOH (say 0.1 mL) increases pH of solution very rapidly as:

Volume of solution = 50 + 50.1 = 100.1 mL

Volume of 0.1N NaOH left unneutralised = 0.1 mL

$$N_1 \times V_1 \equiv N_2 \times V_2$$

$$0.1 \times 0.1 = N_2 \times 100.1$$

or $$N_2 = \frac{0.1 \times 0.1}{100.1} = 10^{-4} \text{ M}$$

$$[OH^-] = 10^{-4} \text{ M}$$

or $$[H^+] = 10^{-10} \text{ M}$$

$\therefore$ $$pH = 10$$

Similarly, $[OH^-]$ and hence $[H^+]$ or pH can be calculated when more and more of NaOH solution has been added. This can easily be calculated from the general formula,

$$[OH^-] = \left(\frac{v - 50}{50 + v}\right) \times 0.1 \text{ N}$$

The values are given in Table 1. It is clear from the table that whereas the first 49.9 mL of NaOH solution added increase the pH only slightly (by about 3 units) but the next 0.2 mL addition (from 49.9 to 51.1 mL) causes a sharp rise in pH from 3.0 to 10.

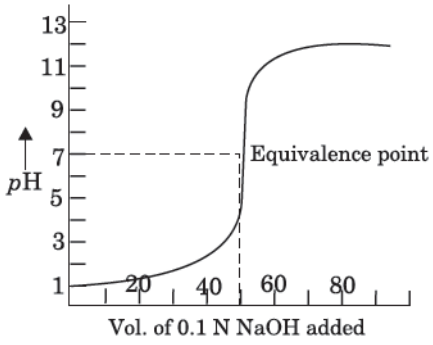

Fig. 1

Choice of a suitable indicator

As already learnt, the indicators show different colour changes in a definite pH range as given ahead (Table 2).

The titration curve for neutralisation of 0.1N HCl with 0.1 N NaOH is shown in Fig. 1. It is clear that there is a sharp jump at pH of 3.3 to 10.7. Thus, any indicator with an effective range between 3.3 to 10.7 may be used for titrating a strong acid with a strong base. For example, indicators

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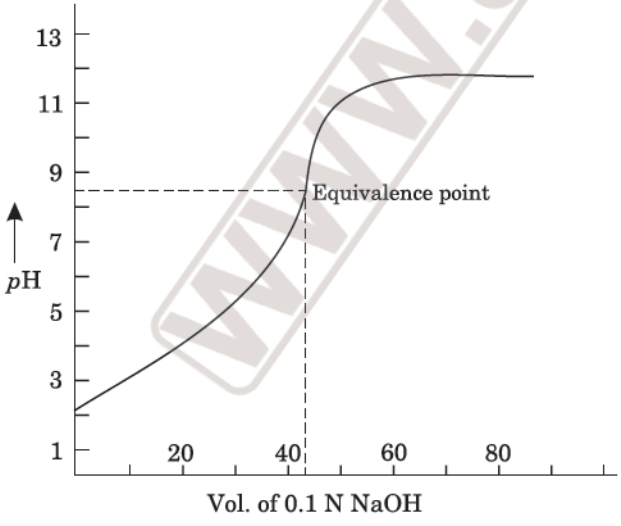
such as methyl orange (pH range 3.1 – 4.4) methyl red (pH range 4.2 – 6.3), bromothymol blue (pH range 6.2 – 7.6) or phenolphthalein (pH range 8.3 – 10) can be used to determine the end point.

Table 2. Indicators and their pH ranges

Indicators	pH range	Colour	
		acid solution	base solution
Thymol blue	1.2 – 2.8	Red	Yellow
Methyl yellow	2.9 – 4.0	Red	Yellow
Methyl orange	3.1 – 4.4	Pink	Yellow
Methyl red	4.2 – 6.3	Red	Yellow
Litmus	5.5 – 7.4	Red	Blue
Bromothymol blue	6.2 – 7.6	Yellow	Blue
Phenol red	6.8 – 8.4	Yellow	Red
Phenolphthalein	8.3 – 10.0	Colourless	Red
Thymolphthalein	9.3 – 10.5	Colourless	Red

Titration of a weak acid with a strong base

Let us consider the titration of 50 mL of 0.1 N CH_3COOH with 0.1 N NaOH. The initial pH of the solution is not 1 because acetic acid is only partially ionized. Initially, the free H^+ ions are neutralised by OH^- ions from NaOH and there is relatively large change in pH. With the addition of more and more NaOH added, the pH increases. The titration curve is shown in Fig. 2. The end point is detected by the inflection in the pH curve. However, the jump in the curve is smaller than in Fig. 1. The equivalence point lies at about pH 8.7 and sharp pH change is observed near the end point where pH changes from 7.7 to 9.7 by the small addition of NaOH. It is, therefore, necessary to use an indicator with a pH range of 7.7 to 9.7. Phenolphthalein (or bromothymol) are the suitable indicators for titration of acetic acid and NaOH.



(Fig. 2)

Similarly, it can be seen that

(*i*) for the titration of weak base like NH_4OH against strong acid like HCl, methyl orange, methyl red or bromothymol blue can be used as indicators.

(*ii*) for the titration of weak acid with weak base, no indicator is found satisfactory. For example, for the titration of 0.1 N acetic acid with 0.1 N NH_4OH, the pH changes during the entire course of titration are gradual. Hence, no sharp end point can be obtained with common indicators. However, a mixed indicator which shows a sharp colour change over a limited pH range may sometimes be used. For example, for the titration of CH_3COOH and NH_4OH, neutral red methylene blue indicator gives satisfactory results.

❑ INDICATOR COLOUR CHANGE INTERVAL

It may be noted that

***(i)* Colour change $pK_{indicator}$ = pH at the equivalence point**

***(ii)* indicators have a useful colour change over a pH range of 2 units.**

These can easily be understood

(*i*) Acid base indicator (HIn) ionizes in aqueous solution as:

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

HIn and In^- have different colours. The equilibrium constant may be represented as:

$$K_{ind} = \frac{[H^+][In^-]}{[HIn]}$$

The actual colour of the indicator depends upon the ratio of concentration of the ionized (In^-) and unionized (HIn) form. The exact colour change will be at the pH when [HIn] = $[In]^-$. Substituting the values in the above relation,

$$K_{ind} = [H^+]$$

or $$-\log K_{ind} = -\log [H^+] \quad \text{or} \quad pK_{in} = pH$$

Thus, for a particular titration, the indicator selected should be such for which pK_{in} = pH of the solution at the equivalence point.

(*ii*) During acid base titration, at any given pH, both forms of the indicators will be present. It is important to realise that human eye has a limited ability to detect the change in colour if the concentration of one coloured form is at least 10 times greater than the concentration of the other

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form. For the indicator,

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

HIn and In^- have different colours. The equilibrium constant,

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \quad ...(i)$$

When $\frac{[HIn]}{[In]}$ =10, the colour of the solution will appear to be due to unionized form (acidic medium).

When $\frac{[In^-]}{[HIn]}$ = 10, the colour of the solution will be due to ionized form *i.e.* alkaline medium.

Rearranging eq. (*i*)

$$[H^+] = \frac{[HIn]}{[In^-]} K_{In}$$

For acidic colour to be visible

$$[H^+] = 10\ K_{In}$$

or $$-\log [H^+] = -\log 10 - \log K_{In}$$

or $$pH = pK_{In} - 1$$

For alkaline colour to be visible

$$[H^+] = \frac{1}{10} K_{In}$$

or $$-\log [H^+] = \log 10 - \log K_{In}$$

or $$pH = PK_{In} + 1.$$

Thus, for colour change of an indicator, $pH = pK_{In} \pm 1$

In other words, pH range for colour change extends over approximately 2 units, one above and one below the pK value of the indicator. Within this range, the indicator changes its colour from one form to another.

OBJECTIVE TYPE QUESTIONS

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Select the Correct Answer :

Equilibrium and Factors Affecting Equilibrium State

A1. For the equilibrium reaction

$$2NO_2(g) \rightleftharpoons N_2O_4(g) + 60.0\ kJ$$

the increase in temperature

(*a*) favours the formation of N_2O_4
(*b*) favours the decomposition of N_2O_4
(*c*) does not effect the equilibrium
(*d*) stops the reaction.

A2. Which of the following will favour the reverse reaction in a chemical equilibrium ?

(*a*) Increasing the concentration of one of the reactants
(*b*) Removal of at least one of the products at regular intervals
(*c*) Increasing the concentration of one or more of the products
(*d*) none of these.

A3. When hydrochloric acid is added to cobalt nitrate solution at room temperature, the following reaction takes place and the reaction mixture becomes blue. On cooling the mixture it becomes pink. On the basis of this information choose the correct answer.

$$\underset{\text{(pink)}}{[Co(H_2O)_6]^{3+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{(blue)}}{[CoCl_4]^{2-}(aq)} + 6H_2O(l)$$

(*a*) $\Delta H > 0$ for the reaction
(*b*) $\Delta H < 0$ for the reaction
(*c*) $\Delta H = 0$ for the reaction
(*d*) The sign of ΔH cannot be predicted on the basis of this information.

A4. In the equilibrium,

$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$$

the equilibrium constant is most likely to be changed by :

(*a*) adding $H_2PO_4^-$ ion (*b*) adding H_3PO_4
(*c*) adding a catalyst (*d*) heating the mixture.

A5. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, if degree of dissociation is α at equilibrium pressure P, then the equilibrium constant for the reaction is :

(*a*) $K_p = \frac{\alpha^2}{1+\alpha^2 P}$ (*b*) $K_p = \frac{\alpha^2 P^2}{1-\alpha^2}$

(*c*) $K_p = \frac{\alpha P^2}{1-\alpha^2}$ (*d*) $K_p = \frac{\alpha^2 P}{1-\alpha^2}$

A6. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, $\Delta H = 110\ kJ$.

The pressure of CO_2 :

(*a*) increases on adding catalyst
(*b*) decreases if T is raised
(*c*) increases if T is raised
(*d*) increases, if an inert gas is passed keeping T constant.

Answers

A1. (*b*) **A2.** (*c*) **A3.** (*a*) **A4.** (*d*) **A5.** (*d*) **A6.** (*c*)

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A7. K_p for the reaction :

$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ is found to be 16 at a given temperature. Originally equal number of moles of H_2 and CO_2 were placed in the flask. At equilibrium, the pressure of H_2 is 1.20 atm. What is the partial pressure of CO and H_2O ?

(*a*) 1.20 atm. each (*b*) 2.40 atm. each

(*c*) 4.80 atm. each (*d*) 9.60 atm. each

A8. An equilibrium mixture for the reaction $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ had 1 mole of hydrogen sulphide, 0.2 mole of H_2 and 0.8 mole of S_2 in 2 litre vessel. The value of K_c is :

(*a*) 0.004 (*b*) 0.080

(*c*) 0.016 (*d*) 0.160

A9. In a system : $A(s) \rightleftharpoons 2B(g) + 3C(g)$ if the concentration of C at equilibrium is increased by a factor of 2, it will cause the equilibrium concentration of B to change to

(*a*) 2 times

(*b*) $\sqrt[3]{2}$ times the original value

(*c*) 1/2 of the original value

(*d*) $\frac{1}{\sqrt[3]{2}}$ times the original value

A10. In a reversible reaction, two substances are in equilibrium. If the concentration of each one is doubled the equilibrium is :

(*a*) reduced to half to its original value

(*b*) reduced to 1/4th of original value

(*c*) doubled (*d*) constant

A11. For the reaction

$CH_4(g + 2O_2(g)) \rightleftharpoons CO_2(g) + 2H_2O(g)$,

$\Delta_r H = -170.8\ kJmol^{-1}$

Which of the following statements is not true?

(*a*) The equilibrium constant for the reaction is given by $K_p = \frac{pCO_2}{pCH_4 \times pO_2}$

(*b*) Addition of $CH_4(g)$ or $O_2(g)$ at equilibrium will cause a shift to the right

(*c*) The reaction is exothermic

(*d*) At equilibrium, the concentrations of $CO_2(g)$ and $H_2O(l)$ are not equal.

A12. In a system :

$A(g) + B(g) + \text{heat} \longrightarrow 2C(s) + 2D(g)$

equilibrium is established. The presence of B valpour is doubled to re-establish the equilibrium. The factor by which D is changed is

(*a*) 2 (*b*) 3

(*c*) $\sqrt{2}$ (*d*) $\sqrt{3}$

A13. For the reversible reaction :

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500°C, the value of K_p is 1.44×10^{-5}, when partial pressure is measured in atmosphere. The corresponding value of K_c with concentration mol litre^{-1} is

(*a*) $1.44 \times 10^{-5}/(0.082 \times 500)^{-2}$

(*b*) $1.44 \times 10^{-5}/(8.314 \times 733)^{-2}$

(*c*) $1.44 \times 10^{-5}/(0.082 \times 773)^{2}$

(*d*) $1.44 \times 10^{-5}/(0.082 \times 773)^{-2}$

A14. For the reaction

$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

the K_p/K_c is equal to

(*a*) $\sqrt{RT}$ (*b*) RT

(*c*) 1/RT (*d*) 1.0

A15. The equilibrium constant (K_p) for the decomposition of gaseous water :

$$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2} O_2(g)$$

is related to degree of dissociation at a total pressure P is given by

(*a*) $K_p = \frac{\alpha^3 P^{1/2}}{(1+\alpha)(2+\alpha)^{1/2}}$ (*b*) $K_p = \frac{\alpha^3 P^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(*c*) $K_p = \frac{\alpha^{3/2} P^2}{(1-\alpha)(2+\alpha)^{1/2}}$ (*d*) $K_p = \frac{\alpha^{3/2} P^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

A16. One mole of $N_2O_4(g)$ at 300 K is kept in a closed vessel at 1 atm pressure. It is heated to 600 K when 20% by mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is

(*a*) 1.2 atm (*b*) 2.4 atm

(*c*) 2.0 atm (*d*) 1.0 atm

A17. The degree of dissociation of N_2O_4 :

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

at temperature T and total pressure P is α. Which of the following expression is corret for the equilibrium constant at this temperature ?

(*a*) $\frac{2\alpha}{1-\alpha^2}$ (*b*) $\frac{\alpha^2 P}{1-\alpha}$

(*c*) $\frac{4\alpha^2}{1-\alpha^2}$ (*d*) $\frac{4\alpha^2 P}{1-\alpha^2}$

Answers

A7. (*c*) **A8.** (*c*) **A9.** (*d*) **A10.** (*d*) **A11.** (*a*) **A12.** (*c*) **A13.** (*d*) **A14.** (*c*) **A15.** (*d*) **A16.** (*b*) **A17.** (*d*)

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Acid-Base Concepts, Dissociation of Acids and Bases and pH of Solutions

A18. The pH of a solution is 5.9. If the hydrogen ion concentration is decreased hundred times, the solution will be :

(*a*) more acidic (*b*) neutral
(*c*) less acidic (*d*) slightly basic

A19. On adding 20 ml of N/10 NaOH solution to 10 ml of N/10 HCl, the resulting solution will :

(*a*) turn blue litmus red
(*b*) turn phenolphthalein solution pink
(*c*) turn methyl orange red
(*d*) will have no effect on red or blue litmus solution

A20. K_a for CH_3COOH is 1.8×10^{-5} and K_b for NH_4OH is 1.8×10^{-5}. The pH of ammonium acetate will be

(*a*) 7.005 (*b*) 4.75
(*c*) 7.0 (*d*) Between 6 and 7

A21. The $[OH^-]$ of an aqueous solution is 1×10^{-5}. The pH of the solution is :

(*a*) 5 (*b*) 9
(*c*) 4.5 (*d*) 11

A22. Which of the following species is amphoteric in nature ?

(*a*) H_3O^+ (*b*) Cl^-
(*c*) HSO_4^- (*d*) CO_3^{2-}

A23. The pH of 0.05 M solution of a strong dibasic acid is :

(*a*) 0.0 (*b*) 1.0
(*c*) 0.2 (*d*) 0.5

A24. *p*OH of H_2O is 7.0 at 298 K. If water is heated at 350 K, which of the following should be true ?

(*a*) pOH will decrease
(*b*) pOH will increase
(*c*) pOH will remain 7.0
(*d*) Concentration of H^+ ions will increase but that of OH^- will decrease.

A25. If K_{sp} of MOH is 1×10^{-10}, then pH of its aqueous solution will be :

(*a*) 3 (*b*) 6
(*c*) 9 (*d*) 12

A26. Which of the following, when mixed, will give a solution with pH greater than 7 ?

(*a*) 0.01 HCl + 0.2 M NaCl
(*b*) 100 ml of 0.2 M H_2SO_4 + 100 ml of 0.3 M NaOH
(*c*) 100 ml of 0.1 M $HC_2H_3O_2$ + 100 ml of 0.1 M KOH
(*d*) 25 ml of 0.1 M HNO_3 + 25 ml of 0.1 M NH_3.

A27. *p*OH of 10^{-8} M solution of NaOH will be :

(*a*) 8 (*b*) between 6 and 7
(*c*) between 7 and 8 (*d*) below 6

A28. The pH of a solution obtained by mixing 50 mL of 0.4 M HCl and 50 mL of 0.2 M NaOH is :

(*a*) –log 2 (*b*) $-\log 2 \times 10^{-1}$
(*c*) 1.0 (*d*) 2.0

A29. The hydrogen ion concentration of a 10^{-8}M HCl aqueous solution at 298 K($K_w = 10^{-14}$) is :

(*a*) 1.0525×10^{-7}M (*b*) 9.525×10^{-8}M
(*c*) 1.0×10^{-8}M (*d*) 1.0×10^{-6}M

Hydrolysis and Buffer Solutions

A30. Which of the following will produce a buffer solution when mixed in equal volumes?

(*a*) 0.1 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl
(*b*) 0.05 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl
(*c*) 0.1 mol dm^{-3} NH_4OH and 0.05 mol dm^{-3} HCl
(*d*) 0.1 mol dm^{-3} CH_3COONa and 0.1 mol dm^{-3} NaOH

A31. The buffer solution comprising of the following has its pH value less than 7.

(*a*) $HCOONH_4$ (*b*) CH_3COONH_4
(*c*) HCOOH + HCOOK (*d*) $NH_4OH + NH_4Cl$

A32. One litre of a buffer solution containing 0.01 M NH_4Cl and 0.1 M NH_4OH having pK_b of 5 has pH of :

(*a*) 9 (*b*) 10
(*c*) 4 (*d*) 6

A33. When a salt of strong base and weak acid is hydrolysed, the resulting solution has :

(*a*) pH = 7 (*b*) pH = 0
(*c*) pH < 7 (*d*) pH > 7

A34. Which of the following pairs constitutes a buffer?

(a) NaOH and NaCl (b) HNO_3 and NH_4NO_3
(c) HCl and KCl (d) HNO_2 and $NaNO_2$

Solubility and Solubility Product

A35. The solubility product of $CaSO_4$ is 6.4×10^{-5}. The solubility of salt in moles/litre is :

(*a*) 8×10^{-16} (*b*) 8×10^{-2}
(*c*) 8×10^{-3} (*d*) 1.6×10^{-3}

A36. If the concentration of CrO_4^{2-} ions in a saturated solution of silver chromate is 2×10^{-4}, solubility product of silver chromate will be :

(*a*) 32×10^{-12} (*b*) 16×10^{-12}
(*c*) 8×10^{-12} (*d*) 4×10^{-8}

Answers

A18. (*c*) **A19.** (*b*) **A20.** (*c*) **A21.** (*b*) **A22.** (*c*) **A23.** (*b*) **A24.** (*a*) **A25.** (*c*) **A26.** (*c*) **A27.** (*b*)
A28. (*c*) **A29.** (*a*) **A30.** (*c*) **A31.** (*c*) **A32.** (*b*) **A33.** (*d*) **A34.** (*d*) **A35.** (*c*) **A36.** (*a*)

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A37. How many grams of CaC_2O_4 will dissolve in distilled water to make one litre of saturated solution ? Solubility product of CaC_2O_4 is 2.5×10^{-9} mole^2 litre^{-2} and its molecular mass is 128.

(*a*) 0.0640 g (*b*) 0.0064 g

(*c*) 0.0128 g (*d*) 0.0032 g

A38. The salt M_xN_y ionizes as :

$$M_xN_y(s) \rightleftharpoons xM^{p+}(aq) + yN^{q-}\ (xp^+ = yq^-)$$

Its solubility may be expressed as :

(*a*) $(K_{sp})^{1/x+y}$ (*b*) $(K_{sp}\ M^x\ N^y)^{x+y}$

(*c*) $(K_{sp}/M^x\ N^y)^{x-y}$ (*d*) $(K_{sp}/M^x\ N^y)^{1/x+y}$

A39. Solubility of BaF_2 in a solution of $Ba(NO_3)_2$ will be represented by the concentration term :

(*a*) $[Ba^{2+}]$ (*b*) $[F^-]$

(*c*) $\frac{1}{2}[F^-]$ (*d*) $2[NO_3^-]$

A40. H_2S gas when passed through solution of cations containing HCl precipitates the cations of second group of qualitative analysis but not those belonging to the fourth group. It is because

(*a*) presence of HCl decreases the sulphide ion concentration

(*b*) sulpides of group IV cations are unstable in HCl

(*c*) solubility product of group II sulphides is more than that of group IV sulphides

(*d*) presence of HCl increase the sulphide ion concentration

A41. The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is '*s*'. The corresponding solubility product is K_{sp}. '*s*' is given in terms of K_{sp} by the relation :

(*a*) $s = (256\ K_{sp})^{1/5}$ (*b*) $s = (128\ K_{sp})^{1/4}$

(*c*) $s = (K_{sp}/128)^{1/4}$ (*d*) $s = (K_{sp}/256)^{1/5}$

Answers

A37. (*b*) **A38.** (*d*) **A39.** (*c*) **A40.** (*a*) **A41.** (*d*)

B MULTIPLE CHOICE QUESTIONS *from Competitive Examinations*

AIPMT & Other State Boards' Medical Entrance

B1. A weak acid, HA has a K_a of 1.00×10^{-5}. If 0.100 mol of this acid is dissolved in one litre of water, the percentage of acid dissociated at equilibrium is closest to

(*a*) 1.00% (*b*) 99.9%

(*c*) 0.100% (*d*) 99.0%

(C.B.S.E. Med. 2007)

B2. If the concentration of OH^- ions in the reaction

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$$

is decreased by 1/4 times, then equilibrium concentration of Fe^{3+} will increase by

(*a*) 8 times (*b*) 16 times

(*c*) 64 times (*d*) 4 times

(C.B.S.E. Med. 2008, Karnataka CET 2016)

B3. The value of equilibrium constant of the reaction :

$$HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + I_2(g) \text{ is } 8.0$$

The equilibrium constant of the reaction,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \text{ will be}$$

(*a*) 1/16 (*b*) 1/64

(*c*) 16 (*d*) 1/8

(C.B.S.E. Med. 2008)

B4. Equal volumes of three acid solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture?

(*a*) 1.11×10^{-4} M (*b*) 3.7×10^{-4} M

(*c*) 3.7×10^{-3} M (*d*) 1.11×10^{-3} M

(C.B.S.E. Med 2008)

B5. K_p and K'_p are equilibrium constants of the two reactions given below

$$\frac{1}{2}N_2(g) + H_2(g) \longrightarrow 2NH_3(g)$$

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

Therefore, K_p and K'_p are related by

(*a*) $K_p = K'^2$ (*b*) $K_p = \sqrt{K'_p}$

(*c*) $K_p = 2K'_p$ (*d*) $K_p = K'_p$

(A.M.U. P.M.T. 2009)

B6. The dissociation constants of acetic acid and HCN at 25°C are 1.5×10^{-4} and 4.5×10^{-10} respectively. The equilibrium constant for the equilibrium

$$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$$

would be

(*a*) 3×10^{-5} (*b*) 3×10^{-4}

(*c*) 3×10^4 (*d*) 3×10^5

(C.B.S.E. PMT 2009)

Answers

B1. (*a*) **B2.** (*c*) **B3.** (*b*) **B4.** (*b*) **B5.** (*b*) **B6.** (*c*)

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B7. The ionisation constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. Hydrolysis constant of ammonium chloride is
(a) 6.5×10^{-12} (b) 5.65×10^{-13}
(c) 5.65×10^{-12} (d) 5.65×10^{-10}
(C.B.S.E.-PMT 2009)

B8. What is the $[OH^-]$ in the final solution prepared by mixing 20 mL of 0.050 M HCl with 30.0 mL of 0.10 M $Ba(OH)_2$?
(a) 0.40 M (b) 0.0050 M
(c) 0.12 M (d) 0.10 M
(C.B.S.E.-PMT 2009)

B9. When solid lead iodide is added to water, the equilibrium concentration of I^- becomes 2.6×10^{-3} M. What is the K_{sp} for PbI_2?
(a) 2.2×10^{-9} (b) 8.8×10^{-9}
(c) 1.8×10^{-8} (d) 35×10^{-8}
(D.U.M.E.T. 2010)

B10. The K_{sp} of $PbCrO_4$ is 1.0×10^{-16}. Then the molar solubility of $PbCrO_4$ is
(a) 1.0×10^{-6} (b) 1.0×10^{-4}
(c) 1.0×10^{-16} (d) 1.0×10^{-8}
(e) 1.0×10^{-12} *(Kerala P.M.T. 2010)*

B11. What is concentration of $[H^+]$ in mol/L of a solution that is 0.20 M in CH_3COONa and 0.10 M in CH_3COOH? K_a for $CH_3COOH = 1.8 \times 10^{-5}$.
(a) 1.8×10^{-5} (b) 9.0×10^{-6}
(c) 3.5×10^{-4} (d) 1.1×10^{-5}
(C.B.S.E. P.M.T. 2010)

B12. In which of the following equilibrium K_c and K_p are not equal?
(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(b) $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$
(c) $2NO(g) \rightleftharpoons N(g) + O_2(g)$
(d) $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
(C.B.S.E. P.M.T. 2010)

B13. In a buffer solution containing equal concentration of B^- and HB, the K_b for B^- is 10^{-10}. The pH of buffer solution is :
(a) 6 (b) 4
(c) 10 (d) 7
(C.B.S.E.P.M.T 2010)

B14. If pH of a saturated solution of $Ba(OH)_2$ is 12, the value of its K_{sp} is :
(a) $5.00 \times 10^{-6} M^3$ (b) $5.00 \times 10^{-7} M^3$
(c) $4.00 \times 10^{-6} M^3$ (d) $4.00 \times 10^{-7} M^3$
(C.B.S.E. P.M.T. 2010)

B15. For the reaction $C(s) + CO_2(g) \longrightarrow 2CO(g)$, $K_p = 63$ atm at 1000 K. If at equilibrium : $P_{CO} = 10\ P_{CO_2}$, then the total pressure of the gases at equilibrium is
(a) 6.3 atm (b) 6.93 atm
(c) 0.63 atm (d) 0.693 atm
(e) 69.3 atm *(Kerala P.M.T. 2011)*

B16. In the reaction $AB(g) \rightleftharpoons A(g) + B(g)$ at 30°C, K_p for the dissociation equilibrium is 2.56×10^{-2} atm. If the total pressure at equilibrium is 1 atm, then the percentage dissociation of AB is
(a) 87% (b) 13%
(c) 43.5% (d) 6%
(e) 16% *(Kerala P.M.T. 2011)*

B17. Which of the following is least likely to behave as Lewis base ?
(a) H_2O (b) NH_3
(c) BF_3 (d) OH^-
(A.I.P.M.T. 2011)

B18. The value of ΔH for the reaction $X_2(g) + 4Y_2(g) \rightleftharpoons 2XY_4(g)$ is less than zero. Formation of $XY_4(g)$ will be favoured at
(a) high temperature and high pressure
(b) low pressure and low temperature
(c) high temperature and low pressure
(d) high pressure and low temperature
(A.I.P.M.T. 2011)

B19. A buffer solution is prepared in which the concentration of NH_3 is 0.30 M and concentration of NH_4^+ is 0.20 M. If equilibrium constant K_b for NH_3 equals 1.8×10^{-5}, what is the pH of the solution ?
(a) 9.08 (b) 9.43
(c) 11.72 (d) 8.72 *(A.I.P.M.T. 2011)*

B20. For the reaction : $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$; the equilibrium constant is K_1. The equilibrium constant is K_2 for the reactions : $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$. What is K for the reaction :

$$NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) ?$$

(a) $\dfrac{1}{(2K_1K_2)}$ (b) $\dfrac{1}{(4K_1K_2)}$
(c) $\left(\dfrac{1}{K_1K_2}\right)^{1/2}$ (d) $\dfrac{1}{K_1K_2}$
(Kerala P.M.T. 2011)

B21. The pK_a of an acid HA is 4.77 and pK_b of a base BOH is 4.75. The pH of 0.1 M aqueous solution of the salt AB is
(a) 7.02 (b) 7.01
(c) 6.99 (d) 7.00
(e) 6.98 *(Kerala P.M.T. 2012)*

Answers

B7. (d) **B8.** (d) **B9.** (b) **B10.** (d) **B11.** (b) **B12.** (b) **B13.** (b) **B14.** (b) **B15.** (b) **B16.** (e)
B17. (c) **B18.** (d) **B19.** (b) **B20.** (c) **B21.** (b)

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B22. Which one of the following will decrease the pH of 50 mL of 0.01 M hydrochloric acid ?
(*a*) Addition of 50 mL of 0.01 M HCl
(*b*) Addition of 50 mL of 0.002 M HCl
(*c*) Addition of 150 mL of 0.002 M HCl
(*d*) Addition of 5 mL of 1 M HCl
(*e*) Addition of metallic zinc *(Kerala P.M.T. 2012)*

B23. pH of a saturated solution of $Ba(OH)_2$ is 12. The value of solubility product (K_{sp}) of $Ba(OH)_2$ is
(*a*) 3.3×10^{-7} (*b*) 5.0×10^{-7}
(*c*) 4.0×10^{-6} (*d*) 5.0×10^{-6}
(A.I.P.M.T. 2012)

B24. Buffer solutions have constant acidity and alkalinity because
(*a*) these give unionised acid or base on reaction with added acid or alkali
(*b*) acids and alkalies in these solutions are shielded from attack by other ions
(*c*) they have large excess of H^+ or OH^- ions
(*d*) they have fixed value of pH *(A.I.P.M.T. 2012)*

B25. The pH of a 0.05 M ammonia solution is 10.97. Find the ionization constant of the conjugate acid of ammonia, NH_4^+
Given $pK_w = 14.0$, K_b for ammonia $= 1.77 \times 10^{-5}$
(*a*) 4.77×10^{-5} (*b*) 9.77×10^{-5}
(*c*) 4.99×10^{-10} (*d*) 5.64×10^{-10}
(A.M.U. Med. 2013)

B26. Which of these is least likely to act as a Lewis base ?
(*a*) BF_3 (*b*) PF_3
(*c*) CO (d) F^- *(NEET 2013)*

B27. For the reaction $2A_3 \rightleftharpoons 3A_2$ the equilibrium constant and the ΔG° values at a certain temperature are respectively 1×10^{30} and -172.4 kJ mol^{-1}. The equilibrium temperature in °C is about
(2.303 R = 19.15 J K^{-1} mol^{-1})
(*a*) 300 (*b*) 27
(*c*) 273 (*d*) 298
(*e*) 270 *(Kerala PMT 2014)*

B28. The pK_a of a weak acid HA and pK_b of a weak base BOH are 4.60 and 4.80 respectively. The pH of 0.1 M solution of the salt, BA, formed from the acid HA and base BOH is
(*a*) 7.10 (*b*) 9.40
(*c*) 6.90 (*d*) 0.20
(*e*) 4.80 *(Kerala PMT 2014)*

B29. For a given exothermic reaction, K_p and K_p' are the equilibrium constants at temperatures T_1 and T_2, respectively. Assuming that heat of reaction is constant in temperature range between T_1 and T_2, it is readily observed that
(*a*) $K_p > K_p'$ (*b*) $K_p < K_p'$
(*c*) $K_p = K_p'$ (*d*) $K_p = 1/K_p'$
(AIPMT 2014)

B30. For the reversible reaction,
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{heat}$
The equilibrium shifts in forward direction
(*a*) by increasing the concentration
(*b*) by decreasing the pressure
(*c*) by decreasing the concentrations of $N_2(g)$ and $H_2(g)$
(*d*) by increasing pressure and decreasing temperature
(AIPMT 2014)

B31. Which of the following salts will give highest pH in water?
(*a*) KCl (*b*) NaCl
(*c*) Na_2CO_3 (*d*) $CuSO_4$
(AIPMT 2014)

B32. Using the Gibb's energy change, $\Delta G^\circ = +63.3$ kJ, for the following reaction,
$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$ the K_{sp} of $Ag_2CO_3(s)$ in water at 25°C is (R = 8.314 J K^{-1} mol^{-1})
(*a*) 3.2×10^{-26} (*b*) 8.0×10^{-12}
(*c*) 2.9×10^{-3} (*d*) 7.9×10^{-2}
(AIPMT 2014)

B33. At 800 K in a sealed vessel, for the equilibrium $N_2(g) + O_2(g), \rightleftharpoons 2NO(g)$, the equilibrium concentrations of $N_2(g)$, $O_2(g)$ and $NO(g)$ are respectively 0.36×10^{-3} M, 4.41×10^{-3} M and 1.4×10^{-3} M. Then, the value of K_C for the reaction $NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at 800 K is
(*a*) 1.1 (*b*) 0.9
(*c*) 3×10^3 (*d*) 9×10^{-3}
(*e*) 0.33 *(Kerala PMT 2015)*

B34. Which one of the following species cannot act as both Bronsted acid and base?
(*a*) H_2O (*b*) HCO_3^-
(*c*) HSO_4^- (*d*) NH_2^-
(*e*) NH_3 *(Kerala PMT 2015)*

B35. The K_{sp} of Ag_2CrO_4, AgCl, AgBr and AgI are respectively, 1.1×10^{-12}, 1.8×10^{-10}, 5.0×10^{-13}, 8.3×10^{-17}. Which one of the following salts will precipitate last if $AgNO_3$ solution is added to the solution containing equal moles of NaCl, NaBr, NaI and Na_2CrO_4?
(*a*) AgBr (*b*) Ag_2CrO_4
(*c*) AgI (*d*) AgCl
(AIPMT 2015)

Answers

B22. (*d*) **B23.** (*b*) **B24.** (*a*) **B25.** (*d*) **B26.** (*a*) **B27.** (*b*) **B28.** (*c*) **B29.** (*a*) **B30.** (*d*) **B31.** (*c*)
B32. (*b*) **B33.** (*b*) **B34.** (*d*) **B35.** (*b*)

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B36. What is the pH of the resulting solution when equal volumes of 0.1 M NaOH and 0.01 M HCl are mixed?
(*a*) 7.0 (*b*) 1.04
(*c*) 12.65 (*d*) 2.0
(*AIPMT 2015*)

B37. Which one of the following pairs of solution is not an acidic buffer?
(*a*) H_2CO_3 and Na_2CO_3
(*b*) H_3PO_4 and Na_3PO_4
(*c*) $HClO_4$ and $NaClO_4$
(*d*) CH_3COOH and CH_3COONa (*AIPMT 2015*)

B38. If the equilibrium constant for
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is K, the equilibrium constant for $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$ will be:
(*a*) K (*b*) K^2
(*c*) $K^{1/2}$ (*d*) $\frac{1}{2}K$
(*AIPMT 2015*)

B39. If the value of equilibrium constant for a particular reaction is 1.6×10^{12}, then at equilibrium the system will contain
(*a*) mostly products
(*b*) similar amounts of reactants and products
(*c*) all reactants
(*d*) mostly reactants (*AIPMT 2015*)

B40. MY and NY_3, two nearly insoluble salts have the same K_{sp} values of 6.2×10^{-13} at room temperature. Which statement would be true in regard to MY and NY_3?
(*a*) The salts MY and NY_3 are more soluble in 0.5 M KY than in pure water.
(*b*) The addition of the salt of KY to solution of MY and NY_3 will have no effect on their solubilities.
(*c*) The molar solubilities of MY and NY_3 in water are identical.
(*d*) The molar solubility of MY in water is less than that of NY_3. (*NEET 2016*)

B41. The percentage of pyridine (C_5H_5N) that forms pyridinium ion ($C_5H_5N^+H$) in a 0.10 M aqueous pyridine solution (K_b for $C_5H_5N = 1.7 \times 10^{-9}$) is
(*a*) 0.0060% (*b*) 0.013%
(*c*) 0.77% (*d*) 1.6% (*NEET 2016*)

B42. The solubility of AgCl(s) with solubility product 1.6×10^{-10} in 0.1 M NaCl solution would be
(*a*) 1.26×10^{-5} M
(*b*) 1.6×10^{-9} M
(*c*) 1.6×10^{-11} M
(*d*) zero (*NEET 2016*)

B43. Which of the following statement is not correct?
(*a*) The value of equilibrium constant is changed in the presence of a catalyst in the reaction at equilibrium.
(*b*) Enzymes mainly catalyse biochemical reactions.
(*c*) Coenzymes increase the catalytic activity of enzyme.
(*d*) Catalyst does not initiate any reaction.
(*NEET 2017*)

B44. The equilibrium constants of the following reactions are:
$N_2 + 3H_2 \rightleftharpoons 2NH_3$; K_1
$N_2 + O_2 \rightleftharpoons 2NO$; K_2
$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$; K_3
The equilibrium constant (K) of the reaction:
$2NH_3 + \frac{5}{2}O_2 \overset{K}{\rightleftharpoons} 2NO + 3H_2O$, will be
(*a*) $K_2K_3^3/K_1$ (*b*) K_2K_3/K_1
(*c*) $K_2^3K_3/K_1$ (*d*) $K_1K_3^3/K_2$
(*NEET 2017, W.B. JEE 2018*)

B45. A 20 litre container at 400 K contains $CO_2(g)$ at pressure 0.4 atm and an excess of SrO (neglect the volume of solid SrO). The volume of container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value, will be:
(Given that: $SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g), K_p = 1.6$ atm)
(*a*) 10 litre (*b*) 4 litre
(*c*) 2 litre (*d*) 5 litre (*NEET 2017*)

B46. Concentration of the Ag^+ ions in a saturated solution of $Ag_2C_2O_4$ is 2.2×10^{-4} mol L^{-1}. Solubility product of $Ag_2C_2O_4$ is
(*a*) 2.66×10^{-12} (*b*) 4.5×10^{-11}
(*c*) 5.3×10^{-12} (*d*) 2.42×10^{-8}
(*NEET 2017*)

B47. Which one of the following conditions will favour maximum formation of the product in the reaction:
$A_2(g) + B_2(g) \rightleftharpoons X_2(g)$, $\Delta_r H = -X$ kJ?
(*a*) Low temperature and high pressure
(*b*) Low temperature and low pressure
(*c*) High temperature and high pressure
(*d*) High temperature and low pressure
(*NEET 2018*)

Answers

B36. (*c*) **B37.** (*c*) **B38.** (*c*) **B39.** (*a*) **B40.** (*d*) **B41.** (*b*) **B42.** (*b*) **B43.** (*a*) **B44.** (*a*) **B45.** (*d*) **B46.** (*c*) **B47** (*a*)

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B48. The solubility of $BaSO_4$ in water is 2.42×10^{-3} gL^{-1} at 298 K. The value of its solubility product (K_{sp}) will be (Given molar mass of $BaSO_4$ = 233 g mol^{-1})

(*a*) 1.08×10^{-10} mol^2 L^{-2}

(*b*) 1.08×10^{-12} mol^2 L^{-2}

(*c*) 1.08×10^{-14} mol^2 L^{-2}

(*d*) 1.08×10^{-8} mol^2 L^{-2} *(NEET 2018)*

B49. Following solutions were prepared by mixing different volumes of NaOH and HCl of different concentrations:

A. 60 mL $\frac{M}{10}$ HCl + 40 mL $\frac{M}{10}$ NaOH

B. 55 mL $\frac{M}{10}$ HCl + 45 mL $\frac{M}{10}$ NaOH

C. 75 mL $\frac{M}{5}$ HCl + 25 mL $\frac{M}{5}$ NaOH

D. 100 mL $\frac{M}{10}$ HCl + 100 mL $\frac{M}{10}$ NaOH

pH of which one of them will be equal to 1?

(*a*) B (*b*) A

(*c*) D (*d*) C *(NEET 2018)*

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B50. Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be :

(*a*) 3.98×10^{-8} (*b*) 3.88×10^{6}

(*c*) 3.68×10^{6} (*d*) 3.98×10^{-6}

(A.I.E.E.E. 2005)

B51. Equal volumes of the following Ca^{2+} and F^- solutions are mixed. In which of the solutions will precipitation occur? (K_{sp} of $CaF_2 = 1.7 \times 10^{-10}$)

(1) 10^{-2} M Ca^{2+} + $10^{-5}MF^-$

(2) 10^{-3} M Ca^{2+} + 10^{-3} MF^-

(3) 10^{-4} M Ca^{2+} + $10^{-2}MF^-$

(4) 10^{-2}M Ca^{2+} + $10^{-3}MF^-$

Select the correct answer using the codes given below:

(*a*) in 4 only (*b*) in 1 and 2

(*c*) in 3 and 4 (*d*) in 2,3 and 4

(*e*) in all *(Kerala P.E.T. 2005)*

B52. The equilibrium constant for the reaction:

$SO_3(g) \rightleftharpoons SO_2(g) + O_2(g)$ is $K_c = 4.9 \times 10^{-2}$

The value of K_c for the reaction:

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ will be

(*a*) 2.40×10^{-3} (*b*) 9.8×10^{-2}

(*c*) 4.9×10^{-2} (*d*) 416 *(A.I.E.E.E. 2006)*

B53. The equilibrium constant for the reaction :

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

is 2×10^{-6} at 185°C. Then the equilibrium constant for the reaction

$$4NO(g) + 2O_2(g) \rightleftharpoons 4NO_2(g)$$

at the same temperature would be

(*a*) 2.5×10^{-5} (*b*) 4×10^{-12}

(*c*) 2.5×10^{11} (*d*) 2×10^{6}

(*e*) 5×10^{5} *(Kerala C.E.T. 2007)*

B54. In a saturated solution of the sparingly soluble strong electrolyte, $AgIO_3$ (molecular mass = 283), the equilibrium which sets in is :

$$AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$$

If the solubility product constant, K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 mL of its saturated solution?

(*a*) 2.83×10^{-3} *g* (*b*) 1.0×10^{-7}g

(*c*) 1.0×10^{-4} *g* (*d*) 28.3×10^{-2} *g*

(A.I.E.E.E. 2007)

B55. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be :

(*a*) 5.0×10^{15} (*b*) 5.0×10^{-15}

(*c*) 0.2×10^{5} (*d*) 5.0×10^{-5}

(A.I.E.E.E. 2007)

B56. The pK_a of a weak acid (HA) is 4.5. The *p*OH of an aqueous buffered solution of HA in which 50% of the acid is ionized is :

(*a*) 2.5 (*b*) 9.5

(*c*) 7.0 (*d*) 4.5 *(A.I.E.E.E. 2007)*

B57. The pH of a solution obtained by mixing 50 mL of 1N HCl and 30 mL of 1 N NaOH is [log 2.5 = 0.3979]

(*a*) 0.979 (*b*) 0.6021

(*c*) 12.042 (*d*) 1.2042

(*e*) 0.3979 *(Kerala P.E.T. 2008)*

B58. For the following three reactions (*i*), (*ii*) and (*iii*), equilibrium constants are given

(*i*) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$; K_1

(*ii*) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$; K_2

(*iii*) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$; K_3

Which of the following relations is correct?

(*a*) $K_3K_2^{\,3} = K_1^{\,2}$ (*b*) $K_1\sqrt{K_2} = K_3$

(*c*) $K_2K_3 = K_1$ (*d*) $K_3 = K_1K_2$

(A.I.E.E.E. 2008)

B59. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be

(*a*) 9.22 (*b*) 9.58

(*c*) 4.79 (*d*) 7.01 *(A.I.E.E.E. 2008)*

Answers

B48. (*a*) **B49.** (*d*) **B50.** (*d*) **B51.** (*d*) **B52.** (*d*) **B53.** (*c*) **B54.** (*a*) **B55.** (*b*) **B56.** (*b*) **B57.** (*b*) **B58.** (*d*) **B59.** (*d*)

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B60. 5 moles of SO_2 and 5 moles of O_2 are allowed to react. At equilibrium, it was found that 60% of SO_2 is used up. If the partial pressure of the equilibrium mixture is 1 atm, the partial pressure of O_2 is

(*a*) 0.52 atm (*b*) 0.41 atm
(*c*) 0.21 atm (*d*) 0.82 atm

(Karnataka C.E.T. 2009)

B61. 30 cc of M/3 HCl, 20 cc of M/2 HNO_3 and 40 cc of M/4 NaOH solutions are mixed and volume was made upto $1dm^3$. The pH of resulting solution is

(*a*) 2 (*b*) 1
(*c*) 3 (*d*) 8

(Karnataka C.E.T. 2009)

B62. Solid $Ba(NO_3)_2$ is gradually dissolved in a 10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form ?

(K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$)

(*a*) 4.1×10^{-5} M
(*b*) 8.1×10^{-8} M
(*c*) 5.1×10^{-5} M
(*d*) 8.1×10^{-7} M *(A.I.E.E.E. 2009)*

B63. 0.1 M HCl and 0.1 M H_2SO_4, each of volume 2 mL are mixed and the volume is made up to 6 mL by adding 2 mL of 0.01 N NaCl solution. The pH of resulting mixture is :

(*a*) 1.17 (*b*) 1.0
(*c*) 0.3 (*d*) log 2 – log 3

(W.B. JEE 2010)

B64. The pH of the solution produced by mixing equal volume of 2.0×10^{-3} M $HClO_4$ and 1.0×10^{-2} M $KClO_4$ is

(*a*) 2.7 (*b*) 2.3
(*c*) 3.0 (*d*) 1.0

(A.M.U. Engg. 2010)

B65. Consider the following reactions in which all the reactants and the products are in gaseous state.

$2PQ \rightleftharpoons P_2 + Q_2$; $K_1 = 2.5 \times 10^5$

$PQ + \frac{1}{2} R_2 \rightleftharpoons PQR$; $K_2 = 5 \times 10^{-3}$

The value of K_3 for the equilibrium

$\frac{1}{2}P_2 + \frac{1}{2}Q_2 + \frac{1}{2}R_2 \rightleftharpoons PQR$, is

(*a*) 2.5×10^{-3} (*b*) 2.5×10^3
(*c*) 1.0×10^{-5} (*d*) 5×10^3
(*e*) 5×10^{-3} *(Kerala P.E.T. 2010)*

B66. In aqueous solution the ionization constants for carbonic acid are :

$K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$

Select the correct statement for a saturated 0.034 M solution of carbonic acid.

(*a*) The concentration of H^+ and HCO_3^- are approximately equal.
(*b*) The concentration of H^+ is double that of CO
(*c*) The concentration of CO is 0.034 M.
(*d*) The concentration of CO is greater than that of HCO. *(A.I.E.E.E. 2010)*

B67. At 25°C, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions?

(*a*) 1 (*b*) 8
(*c*) 9 (*d*) 10 *(A.I.E.E.E. 2010)*

B68. Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is :

(*a*) 6.2×10^{-5} g (*b*) 5.0×10^{-8} g
(*c*) 1.2×10^{-10} g (*d*) 1.2×10^{-9} g

(A.I.E.E.E. 2010)

B69. If the equilibrium constants of the following equilibria

$$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3 \text{ and}$$

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$

are given by K_1 and K_2 respectively, which of the following reactions are correct ?

(*a*) $K_2 = \left(\frac{1}{K_1}\right)^2$ (*b*) $K_1 = \left(\frac{1}{K_1}\right)^3$

(*c*) $K_2 = \left(\frac{1}{K_1}\right)$ (*d*) $K_2 = (K_1)^2$ *(W.B. J.E.E. 2011)*

B70. The solubility of $Ca_3(PO_4)_2$ in water is y moles/litre. Its solubility product is

(*a*) $6y^4$ (*b*) $36y^4$
(*c*) $64y^5$ (*d*) $108y^5$

(W.B. J.E.E. 2011)

Answers

B60. (*b*) **B61.** (*a*) **B62.** (*c*) **B63.** (*b*) **B64.** (*c*) **B65.** (*c*) **B66.** (*a*) **B67.** (*d*) **B68.** (*d*) **B69.** (*a*) **B70.** (*d*)

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B71. For a concentrated solution of a weak electrolyte A_xB_y, the degree of dissociation is given as

(a) $\alpha = \sqrt{K_{eq}/C(x+y)}$ (b) $\alpha = \sqrt{K_{eq}C/(xy)}$

(c) $\alpha = (K_{eq}/C^{x+y-1}x^xy^y)^{1/(x+y)}$ (d) $\alpha = \sqrt{K_{eq}/xyC}$

(A.M.U. Engg. 2011)

B72. The solubility product (K_{sp}) of the following compounds are given at 25°C

Compound	K_{sp}
AgCl	1.1×10^{-10}
AgI	1.0×10^{-16}
$PbCrO_4$	4.0×10^{-14}
Ag_2CO_3	8.0×10^{-12}

The most soluble and least soluble compounds are respectively

(a) AgCl and $PbCrO_4$ (b) AgI and Ag_2CO_3

(c) AgCl and Ag_2CO_3 (d) Ag_2CO_3 and AgI

(e) Ag_2CO_3 and $PbCrO_4$ *(Kerala P.E.T. 2011)*

B73. Four moles of PCl_5 are heated in a closed 4 dm^3 container to reach equilibrium at 400 K. At equilibrium 50% of PCl_5 is dissociated. What is the value of K_c for the dissociation of PCl_5 into PCl_3 and Cl_2 at 400 K ?

(a) 0.50 (b) 1.00

(c) 1.25 (d) 0.05

(e) 0.25 *(Kerala P.E.T. 2011)*

B74. pH value of which one of the following is NOT equal to one?

(a) 0.1 M CH_3COOH

(b) 0.1 M HNO_3

(c) 0.05 M H_2SO_4

(d) 50 cm^3 0.4 M HCl + 50 cm^3 0.2 M NaOH

(Karnataka C.E.T. 2011)

B75. A buffer solution contains 0.1 mole of sodium acetate dissolved in 1000 cm^3 of 0.1 M acetic acid. To the above buffer solution, 0.1 mole of sodium acetate is further added and dissolved. The pH of the resulting buffer is

(a) pK_a (b) $pK_a + 2$

(c) $pK_a - \log 2$ (d) $pK_a + \log 2$

(Karnataka C.E.T. 2011)

B76. H_2S is passed into one dm^3 of a solution containing 0.1 mole of Zn^{2+} and 0.01 mole of Cu^{2+} till the sulphide ion concentration reaches 8.1×10^{-19} moles. Which one of the following statements is true ?

[K_{sp} of ZnS and CuS are 3×10^{-22} and 8×10^{-36} respectively]

(a) Only ZnS precipitates

(b) Both CuS and ZnS precipitate

(c) Only CuS precipitates

(d) No precipitation occurs *(Karnataka C.E.T. 2011)*

B77. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is

(a) 1.8 atm (b) 3 atm

(c) 0.3 atm (d) 0.18 atm

(A.I.E.E.E. 2011)

B78. The K_{sp} of $Cr(OH)_3$ is 1.6×10^{-30}. The molar solubility of the compound in water is

(a) $\sqrt[3]{1.6 \times 10^{-30}}$

(b) $\sqrt[4]{1.6 \times 10^{-30}/27}$

(c) $1.6 \times 10^{-30}/27$

(d) $\sqrt[2]{1.6 \times 10^{-30}}$ *(A.I.E.E.E. 2011)*

B79. An acid HA ionises as

$$HA \rightleftharpoons H^+ + A^-$$

The pH of 1.0 M solution is 5. Its dissociation constant would be

(a) 5 (b) 5×10^{-8}

(c) 1×10^{-5} (d) 1×10^{-10}

(A.I.E.E.E. 2011)

B80. A 100 mL 0.1 M solution of ammonium acetate is diluted by adding 100 mL of water. The pH of the resulting solution will be (pK_a of acetic acid is nearly equal to pK_a of NH_4OH)

(a) 4.9 (b) 5.0

(c) 7.0 (d) 10.0

(W.B. J.E.E. 2012)

B81. For $Fe(OH)_3$ the solubility product K_{sp} is (if s is the solubility)

(a) 27 s^4 (b) s^2

(c) $4s^3$ (d) $8s^4$

(Odisha J.E.E. 2012)

B82. A buffer solution is prepared by mixing equal concentration of weak base and its salt with strong acid. For the base K_b is given as 10^{-9}. The pH of the buffer solution is

(a) 3 (b) 5

(c) 8 (d) 9

(Odisha J.E.E. 2012)

Answers

B71. (c) **B72.** (d) **B73.** (a) **B74.** (a) **B75.** (d) **B76.** (b) **B77.** (a) **B78.** (b) **B79.** (d) **B80.** (c) **B81.** (a) **B82.** (b)

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B83. In the following equilibrium reaction,

$$2A \rightleftharpoons B + C$$

the equilibrium concentrations of A, B and C are 1×10^{-3} M, 2×10^{-3} M and 3×10^{-3} M respectively at 300 K. The value of K_c for this equilibrium at the same temperature is

(a) $\frac{1}{6}$ (b) 6

(c) $\frac{1}{36}$ (d) 36

(e) $\frac{1}{24}$ *(Kerala P.E.T. 2012)*

B84. The pH of the solution obtained by mixing 100 mL of a solution of pH = 3 with 400 mL of a solution of pH = 4 is

(a) 3 – log 2.8 (b) 7 – log 2.8

(c) 4 – log 2.8 (d) 5 – log 2.8

(Karnataka C.E.T. 2012)

B85. 5 mL of 0.4 N NaOH is mixed with 20 mL of 0.1 N HCl. The pH of the resulting solution will be

(a) 6 (b) 7

(c) 8 (d) 5

(Karnataka C.E.T. 2012)

B86. On adding which of the following, the pH of 20 mL of 0.1 N HCl will not alter ?

(a) 1 mL of 1 N HCl

(b) 20 mL of distilled water

(c) 1 mL of 0.1 N NaOH

(d) 500 mL of HCl of pH = 1

(Karnataka C.E.T. 2012)

B87. The number of moles of $Ca(OH)_2$ that must be dissolved to make 250 mL solution in water of pH = 10.65 is

(a) 5.6×10^{-5} (b) 6.5×10^{-5}

(c) 4.5×10^{-5} (d) 5.4×10^{-5}

(A.M.U. Engg. 2012)

B88. The equilibrium constant (K_c) for the reaction $N_2(g) + O_2(g) \rightarrow 2NO\ (g)$ at temperature T is 4×10^{-4}. The value of K_c for the reaction,

$$NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$$

at the same temperature is

(a) 2.5×10^2 (b) 4×10^{-4}

(c) 50.0 (d) 0.02

(A.I.E.E.E. 2012)

B89. The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, K_a of this acid is

(a) 1×10^{-3} (b) 1×10^{-5}

(c) 1×10^{-7} (d) 3×10^{-1}

(A.I.E.E.E. 2012)

B90. 1×10^{-3} mole of HCl is added to a buffer solution made up of 0.01 M acetic acid and 0.01 M sodium acetate. The final pH of the buffer will be (given, pK_a of acetic acid is 4.75 at 25° C)

(a) 4.60 (b) 4.66

(c) 4.75 (d) 4.8

(W.B. J.E.E. 2013)

B91. The pH of 10^{-8} M HCl solution is

(a) 8 (b) 6.9586

(c) more than 8 (d) slightly more than 7

(Karnataka C.E.T. 2013)

B92. The sum of pH and pK_b for a basic buffer solution is 13. The ratio of the concentration of the base to that of the salt is

(a) 10 (b) 1

(c) 0.05 (d) 0.1

(e) 20 *(Kerala P.E.T. 2013)*

B93. Two equilibria, $AB \rightleftharpoons A^+ + B^-$ and $AB + B^- \rightleftharpoons AB_2^-$ are simultaneously maintained in a solution with equilibrium constants, K_1 and K_2 respectively. The ratio of $[A^+]$ to $[AB_2^-]$ in the solution is

(a) directly proportional to $[B^-]$

(b) inversely proportional to $[B^-]$

(c) directly proportional to the square of $[B^-]$

(d) inversely proportional to the square of $[B^-]$

(e) independent of $[B^-]$ *(Kerala P.E.T. 2013)*

B94. 100 mL of 1N H_2SO_4 is mixed with 100 mL of 1M NaOH solution. The resulting solution will be

(a) highly acidic (b) neutral

(c) highly basic (d) slightly acidic

(J.K.C.E.T. 2013)

B95. The pH of a saturated solution of a metal hydroxide of formula $X(OH)_2$ is 12.0 at 298 K. What is the solubility product of the metal hydroxide at 298 K (in $mol^3\ L^{-3}$) ?

(a) 2×10^{-6} (b) 1×10^{-7}

(c) 5×10^{-5} (d) 2×10^{-5}

(e) 5×10^{-7} *(Kerala PET 2014)*

B96. In a closed cylinder of capacity 24.6 L the following reaction occurs at 27°C,

$$A_2(s) \rightleftharpoons B_2(s) + 2C(g)$$

At equilibrium 1 g of $B_2(s)$ (molar mass = 50 g mol^{-1}) is present. The equilibrium constant K_p for the equilibrium in atm^2 unit is (R = 0.082 L atm K^{-1} mol^{-1})

(a) 1.6×10^{-2} (b) 1.6×10^{-5}

(c) 1.6×10^{-3} (d) 1.6×10^{-4}

(e) 1.6×10^{-1} *(Kerala PET 2014)*

Answers

B83. (b) **B84.** (c) **B85.** (b) **B86.** (d) **B87.** (a) **B88.** (c) **B89.** (b) **B90.** (b) **B91.** (b) **B92.** (d) **B93.** (d) **B94.** (b) **B95.** (e) **B96.** (c)

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B97. The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. What is its pH?
(*a*) 3.84 (*b*) 2.42 (*c*) 4.44 (*d*) 1.42
(J.K. CET 2014)

B98. What shall be the pH of a solution formed by mixing 10 mL of 0.1 M H_2SO_4 and 10 mL of N/10 KOH?
(*a*) 11.40 (*b*) 8.64 (*c*) 3.0 (*d*) 7.00
(A.M.U. Engg. 2014)

B99. What will be the solubility product of $Ca(OH)_2$ if its solubility is $\sqrt{3}$.
(*a*) 3 (*b*) $3\sqrt{3}$ (*c*) $12\sqrt{3}$ (*d*) 27
(AMU Engg. 2014)

B100. For the reaction $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$, if $K_p = K_c(RT)^x$ where the symbols have usual meaning then the value of x is (assuming ideality)
(*a*) 1 (*b*) –1
(*c*) $-\frac{1}{2}$ (*d*) $\frac{1}{2}$ *(JEE Main 2014)*

B101. For the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ at 300 K, the value of ΔG° is –690.9 R. The equilibrium constant value for the reaction at that temperature is (R is gas constant)
(*a*) 10 atm^{-1} (*b*) 10 atm
(*c*) 10 (*d*) 1 *(WB JEE 2015)*

B102. The ratio of volumes of CH_3COOH 0.1 (N) to CH_3COONa 0.1 (N) required to prepare a buffer solution of pH 5.74 is (given : pK_a of CH_3COOH is 4.74)
(*a*) 10 : 1 (*b*) 5 : 1 (*c*) 1 : 5 (*d*) 1 : 10
(WB JEE 2015)

B103. The standard Gibbs energy change at 300 K for the reaction $2A \rightleftharpoons B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is [A] = $\frac{1}{2}$, [B] = 2 and [C] = $\frac{1}{2}$. The reaction proceeds in the [R = 8.314 J/K/mol, e = 2.718]
(*a*) forward direction because $Q < K_C$
(*b*) reverse direction bacause $Q < K_C$
(*c*) forward direction bacause $Q > K_C$
(*d*) reverse direction bacause $Q > K_C$
(JEE Main 2015)

B104. How many times a 0.1 M strong monobasic acid solution should be diluted so that pH of the resulting solution is tripled?
(*a*) 50 (*b*) 10 (*c*) 25 (*d*) 100 (*e*) 1000
(Kerala PET 2016)

B105. The equilibrium pressure for the reaction $MSO_4 . 2H_2O(s) \rightleftharpoons MSO_4(s) + 2H_2O(g)$ is $\pi/4$ atm at 400 K. The K_p for the given reaction (in atm^2) is
(*a*) $\pi^2/4$ (*b*) $\pi/6$
(*c*) $\pi^2/16$ (*d*) $\pi/16$
(*e*) $16/\pi$ *(Kerala PET 2016)*

B106. In the reaction; $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$, if the concentration of OH^- ions is decreased by $\frac{1}{4}$ times, then the equilibrium concentration of Fe^{3+} will increase by
(*a*) 8 times (*b*) 16 times
(*c*) 64 times (*d*) 4 times
(Karnataka CET 2016)

B107. Equilibrium constants K_1 and K_2 for the following equilibria:
(1) $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$
(2) $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$
are related as:
(*a*) $K_1 = \sqrt{K_2}$ (*b*) $K_2 = \frac{1}{K_1}$
(*c*) $K_1 = 2K_2$ (*d*) $K_2 = \frac{1}{K_1^2}$
(Karnataka CET 2016)

B108. The equilibrium constant at 298 K for a reaction. $A + B \rightleftharpoons C + D$ is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in mol L^{-1}) will be
(*a*) 0.182 (*b*) 0.818 (*c*) 1.818 (*d*) 1.182
(JEE Main 2016)

B109. Equilibrium constants for the following reactions at 1200 K are given:
$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$; $K_1 = 6.4 \times 10^{-8}$
$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$; $K_2 = 1.6 \times 10^{-6}$
The equilibrium constant for the reaction
$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$ at 1200 K will be
(*a*) 0.05 (*b*) 20
(*c*) 0.2 (*d*) 5.0 *(WB JEE 2017)*

B110. The reaction quotient, 'Q_c' is useful in predicting the direction of the reaction. Which of the following is incorrect?
(*a*) If $Q_c > K_c$, the reverse reaction is favoured.
(*b*) If $Q_c < K_c$, the forward reaction is favoured.
(*c*) If $Q_c > K_c$, forward reaction is favoured.
(*d*) If $Q_c = K_c$, no reaction occurs.
(Karnataka CET 2017)

Answers

B97. (*b*) **B98.** (*c*) **B99.** (*c*) **B100.** (*c*) **B101.** (*a*) **B102.** (*d*) **B103.** (*d*) **B104.** (*d*) **B105.** (*c*) **B106.** (*c*) **B107.** (*d*) **B108.** (*c*) **B109.** (*d*) **B110.** (*c*)

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B111. The equilibrium constant for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is 4×10^{-4} at 2000 K.
In presence of a catalyst, the equilibrium is attained ten times faster. Therefore, the equilibrium constant in presence of catalyst at 2000 K is
(a) 4×10^{-3} (b) 40×10^{-4}
(c) 4×10^{-4} (d) 4×10^{-2}
(Karnataka CET 2017)

B112. For the process,
$\frac{3}{2}A \longrightarrow B$, at 298 K, ΔG° is 163 kJ mol^{-1}. The composition of the reaction mixture is [B] = 1 and [A] = 10000. Predict the direction of the reaction and the relation between reaction quotient (Q) and the equilibrium constant (K).
(a) Forward direction because Q > K
(b) Reverse direction because Q > K
(c) Forward direction because Q < K
(d) Reverse direction because Q < K
(e) It is at equilibrium as Q = K
(Kerala PET 2017)

B113. Dissolving NaCN in de–ionised water will result in a solution having
(a) pH < 7 (b) pH = 7
(c) pOH = 7 (d) pH > 7
(WB JEE 2017)

B114. Solubility product (K_{sp}) of saturated $PbCl_2$ in water is 1.8×10^{-4} mol^3 dm^{-9}. What is the concentration of Pb^{2+} in the solution?
(a) $(0.45 \times 10^{-4})^{1/3}$ mol dm^{-3}
(b) $(1.8 \times 10^{-4})^{1/3}$ mol dm^{-3}
(c) $(0.9 \times 10^{-4})^{1/3}$ mol dm^{-3}
(d) $(2.0 \times 10^{-4})^{1/3}$ mol dm^{-3}
(e) $(2.45 \times 10^{-4})^{1/3}$ mol dm^{-3} *(Kerala PET 2017)*

B115. pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is
(a) 7.2 (b) 6.9
(c) 7.0 (d) 1.0 *(JEE Main 2017)*

B116. What will be the equilibrium constant of the given reaction carried out in a 5 L vessel and having equilibrium amounts of A_2 and A as 0.5 mol and 2×10^{-6} mol respectively?
The reaction: $A_2 \rightleftharpoons 2A$
(a) 0.16×10^{-11} (b) 0.25×10^{5}
(c) 0.4×10^{-5} (d) 0.2×10^{-11}
(J.K. CET 2018)

B117. A sample of HI(g) is placed in a flask at a pressure of 0.2 atm. At equilibrium, partial pressure of HI(g) is 0.04 atm. What is K_p for the given equilibrium?
$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
(a) 0.04 (b) 0.4
(c) 40 (d) 4 *(J.K. CET 2018)*

B118. What will be the expression of K_p for the given reaction if the total pressure inside the vessel is P and degree of dissociation of the reactant is α?
The reaction: $N_2O_4 \rightleftharpoons 2NO_2$
(a) $4\alpha^2P/(1 + \alpha^2)$ (b) $4\alpha^2P/(1 - \alpha^2)$
(c) $\alpha^2P/(1 - \alpha^2)$ (d) $\alpha^2/(1 - \alpha)$
(J.K. CET 2018)

B119. In a reaction $A + B \rightleftharpoons C + D$, Le Chateliers principle asserts that an equilibrium between A and B producing C and D can be shifted towards C and D by
(*i*) increasing the concentration of A or B
(*ii*) increasing the concentration of C or D
(*iii*) decreasing the concentration of A or B.
(a) (*ii*) only
(b) Both (*i*) and (*ii*)
(c) (*iii*) only
(d) (*i*) only *(J.K. CET 2018)*

B120. The relationship between K_p and K_c is $K_p = K_c(RT)^{\Delta n}$. What would be the value of Δn for the reaction :
$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
(a) 1 (b) 0.5
(c) 1.5 (d) 2
(Karnataka CET 2018)

B121. Acidity of BF_3 can be explained on which of the following concepts?
(a) Arrhenius concept
(b) Bronsted Lowry concept
(c) Lewis concept
(d) Bronsted Lowry as well as Lewis concept.
(Karnataka CET 2018)

B122. An aqueous solution contains 0.10 M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS^- from H_2S is 1.0×10^{-7} and that of S^{2-} from HS^- ions is 1.2×10^{-13}, then the concentration of S^{2-} ions in aqueous solution is:
(a) 5×10^{-8} (b) 3×10^{-20}
(c) 6×10^{-21} (d) 5×10^{-19}.
(JEE Main 2018)

Answers

B111. (c) **B112.** (b) **B113.** (d) **B114.** (a) **B115.** (b) **B116.** (a) **B117.** (d) **B118.** (b) **B119.** (d) **B120.** (d) **B121.** (c) **B122.** (b)

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B123. An aqueous solution contains an unknown concentration of Ba^{2+}. When 50 mL of a 1 M solution of Na_2SO_4 is added, $BaSO_4$ just begins to precipitate. The final volume is 500 mL. The solubility product of $BaSO_4$ is 1×10^{-10}. What is the original concentration of Ba^{2+}?

(*a*) 5×10^{-9} M (*b*) 2×10^{-9} M
(*c*) 1.1×10^{-9} M (*d*) 1.0×10^{-10} M.

(JEE Main 2018)

B124. Which of the following salt is the most basic in aqueous solution?

(*a*) $Al(CN)_3$ (*b*) CH_3COOK
(*c*) $FeCl_3$ (*d*) $Pb(CH_3COO)_2$.

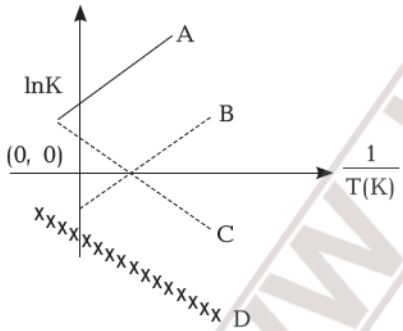
(JEE Main 2018)

B125. An alkali is titrated against an acid with methyl orange as indicator. Which of the following is a correct combination?

	Base	Acid	End point
(*a*)	Weak	Strong	Colourless to pink
(*b*)	Strong	Strong	Pinkish red to yellow
(*c*)	Weak	Strong	Yellow to pinkish red
(*d*)	Strong	Strong	Pink to colourless

(JEE Main 2018)

B126. Which of the following lines correctly show the temperature dependence of equilibrium constant K, for an exothermic reaction?



(*a*) A and B (*b*) B and C
(*c*) C and D (*d*) A and D

(JEE Main 2018)

B127. In a chemical reaction $A + 2B \underset{}{\overset{K}{\rightleftharpoons}} 2C + D$, the initial concentration of B was 1.5 times of the concentration of A, but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant (K) for the aforesaid chemical reaction is

(*a*) 1 (*b*) 16 (*c*) 4 (*d*) $\frac{1}{4}$

(JEE Main 2019)

B128. If K_{sp} of Ag_2CO_3 is 8×10^{-12}, the molar solubility of Ag_2CO_3 in 0.1 M $AgNO_3$ is :

(*a*) 8×10^{-12} M (*b*) 8×10^{-10} M
(*c*) 8×10^{-11} M (*d*) 8×10^{-13} M

(JEE Main 2019)

JEE(Advance) for IIT Entrance

B129. A solution of 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and H^{2+}. is heated with 10^{-16} M sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-2} 10 and 10^{-54} respectively which one will precipitate first ?

(*a*) FeS (*b*) MnS
(*c*) HgS (*d*) ZnS *(I.I.T. 2003)*

B130. A weak acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The precentage hydrolysis of 0.1 M solution of NaX is

(*a*) 0.0001% (*b*) 0.01%
(*c*) 0.1% (*d*) 0.15% *(I.I.T. 2004)*

B131. 0.1 mol of CH_3NH_2 ($K_b = 5.0 \times 10^{-4}$) is mixed with 0.08 mol of HCl and diluted to one litre. What will be the H^+ ion concentration in the solution ?

(*a*) 8×10^{-2} M (*b*) 8×10^{-11}M
(*c*) 1.6×10^{-11} M (*d*) 8×10^{-5} M

(I.I.T. 2005)

B132. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+$; $K_f = 6.8 \times 10^3$
$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $K_f = 1.6 \times 10^3$
Overall formation constant of the complex $[Ag(NH_3)_2]^+$ would be

(*a*) 1.08×10^7 (*b*) 1.08×10^3
(*c*) 6.8×10^6 (*d*) 6.8×10^7 *(I.I.T. 2006)*

B133. 2.5 mL of 2/5 M weak monoacidic base ($K_b = 10^{-12}$ at 25°C) is titrated with 2/15 M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 10^{-14}$ at 25°C)

(*a*) 3.7×10^{-13} M (*b*) 3.2×10^{-7} M
(*c*) 3.2×10^{-2} M (*d*) 2.7×10^{-2} M

(I.I.T. J.E.E. 2008)

B134. Solubility product constants (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature T are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15} respectively. Solubility (mol/dm^3) of salts at temperature T are in order

(*a*) $MX > MX_2 > M_3X$ (*b*) $M_3X > MX_2 > MX$
(*c*) $MX_2 > M_3X > MX$ (*d*) $MX > M_3X > MX_2$

(I.I.T. J.E.E. 2008)

B135. How many litres of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2?

(*a*) 9.0 L (*b*) 0.1 L
(*c*) 0.9 L (*d*) 2.0 L

(J.E.E. Advanced 2013)

B136. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is

(*a*) 1.1×10^{-11} (*b*) 1.1×10^{-10}
(*c*) 1.1×10^{-12} (*d*) 1.1×10^{-9}

(J.E.E. Advanced 2013)

Answers

B123. (*c*) **B124.** (*b*) **B125.** (*c*) **B126.** (*a*) **B127.** (*c*) **B128.** (*b*) **B129.** (*c*) **B130.** (*b*) **B131.** (*b*) **B132.** (*a*) **B133.** (*c*) **B134.** (*d*) **B135.** (*a*) **B136.** (*b*)

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C MULTIPLE CHOICE QUESTIONS
with more than one correct answers

C1. In which of the following reactions, increase in temperature as well as decrease in pressure shift the equilibrium towards the forward direction?

(*a*) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +ve$

(*b*) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $\Delta H = +ve$

(*c*) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = +ve$

(*d*) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -ve$

C2. Which of the following factors favour the reaction:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -93.6$ kJ

(*a*) increase in pressure

(*b*) increase in temperature

(*c*) increase in volume

(*d*) decrease in temperature

C3. Which of the following behave both as Bronsted acids as well Bronsted bases?

(*a*) H_2O (*b*) H_3PO_4

(*c*) HCO_3^- (*d*) HCOOH

C4. Which of the following are Lewis acids?

(*a*) Ag^+ (*b*) $[SiF_6]^{2-}$ (*c*) CO_2 (*d*) O^{2-}

C5. Which of the following aqueous solutions are acidic ?

(*a*) $CuSO_4$ (*b*) CH_3COONH_4

(*c*) $AlCl_3$ (*d*) Na_2CO_3

C6. Which of the following statements are correct?

(*a*) The pH of 1×10^{-8} M HCl solution is 8.

(*b*) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}

(*c*) Autoprotolysis constant of water increases with temperature

(*d*) When a solution of weak monoprotic acid is titrated against a strong base, at half neutralisation point, pH = 1/2 pK_a.

C7. Which of the following statements are not correct?

(*a*) For precipitation to occur, ionic product must be greater than K_{sp}.

(*b*) Buffer solutions resist changes in pH on addition of small amount of acid or base.

(*c*) A solution having pH 6 is more acidic than a solution having pH 5.

(*d*) pH of 1.0 M NaCl is 8.

C8. A buffer solution can be prepared from a mixture of

(*a*) sodium acetate and acetic acid in water.

(*b*) sodium acetate and hydrochloric acid in water

(*c*) ammonia and ammonium chloride in water

(*d*) ammonia and sodium hydroxide in water.

C9. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the value of K is 50 at 400 K and 1700 at 500 K. Which of the following options is/are correct?

(*a*) The reaction is endothermic

(*b*) The reaction is exothermic

(*c*) If $NO_2(g)$ and $N_2O_4(g)$ are mixed at 400 K at partial pressure 20 bar and 2 bar respectively, more $N_2O_4(g)$ will be formed.

(*d*) The entropy of the system increases.

C10. The thermal dissociation equilibrium of $CaCO_{3(s)}$ is studied under different conditions.

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

For this equilibrium, the correct statement(*s*) is (are)

(*a*) ΔH is dependent on T

(*b*) K is independent of the initial amount of $CaCO_3$

(*c*) K is dependent on the pressure of CO_2 at a given T

(*d*) ΔH is independent of the catalyst, if any.

C11. In which of the following mixed aqueous solutions pH = pK_a at equilibrium?

(1) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M CH_3COONa

(2) 100 mL of 0.1 M CH_3COOH + 50 mL of 0.1 M NaOH

(3) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NaOH

(4) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NH_3

(*a*) (1) is correct (*b*) (2) is correct

(*c*) (3) is correct (*d*) both (1) and (2) are correct

(WB JEE 2016)

Answers

C1. (*a, b*) **C2.** (*a, d*) **C3.** (*a, c*) **C4.** (*a, c*) **C5.** (*a, c*) **C6.** (*b, c*) **C7.** (*c, d*) **C8.** (*a, c*) **C9.** (*a, c, d*) **C10.** (*a, b, d*) **C11.** (*a, b, d*)

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D MULTIPLE CHOICE QUESTIONS
based on the given passage/comprehension

Passage I.

For the sparingly soluble salts, an equilibrium is established between the undissolved solid salt and ions of the dissolved salt. For a solution of the salt like $A_x B_y$.

$$A_x B_y = x A^{y+} + y B^{x-}$$
$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

For precipitation to occur, the ionic product must be greater than K_{sp}.

Answer the following questions:

D1. The solubility of A_2X_3 is y mol dm^{-3}. Its solubility product is

(a) $6y^4$ (b) $64y^4$
(c) $36\,y^5$ (d) $108\,y^5$

D2. When equal volume of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with

(a) 10^{-4} M (Ag^+) and 10^{-4} M(Cl^-)
(b) 10^{-5} M (Ag^+) and 10^{-5} M(Cl^-)
(c) 10^{-10}M (Ag^+) and 10^{-6}M(Cl^-)
(d) 10^{-10}M (Ag^+) and 10^{-10} M(Cl^-)

D3. A solution of 10^{-3} M each in Mn^{2+}, Fe^{2+} Zn^{2+} and Hg^{2+} is treated with 10^{-16} M S^{2-} ions. If K_{sp} of MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively, which one will precipitate first

(a) FeS (b) HgS
(c) HgS (d) ZnS

D4. K_{sp} for A_2B_3 salt is 1.1×10^{-23}. Its solubility is

(a) 1×10^{-8} (b) 1×10^{-5}
(c) 1×10^{-6} (d) 1×10^{-7}

D5. What is the minimum concentration of OH^- ions required to precipitate $Fe(OH)_3$ from a 0.001 M solution of $FeCl_3$ (K_{sp} of $Fe(OH)_3 = 1 \times 10^{-36}$).

(a) 1×10^{-12} (b) 1×10^{-11}
(c) 1×10^{-18} (d) 1×10^{-16}

Passage II

pH of a solution of salt of weak acid and weak base is:

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - pK_b$$

and that of weak acid and strong base is

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log c$$

Answer the following questions:

D6. The pH of 0.1 M sodium acetate (K_a for $CH_3COOH = 1.8 \times 10^{-5}$) is

(a) 8.87 (b) 9.36
(c) 4.86 (d) 7.20

D7. For a salt of weak acid and weak base having $K_a = K_b$, the pH at 25°C will be

(a) 7 (b) 14
(c) 0 (d) 1

D8. pH of 0.1 M solution of ammonium cyanide ($pK_a = 9.02$ and $pK_b = 4.76$) is

(a) 13.78 (b) 2.26
(c) 9.13 (d) 8.13

D9. When concentration of ammonium acetate (having $K_a = K_b = 1.8 \times 10^{-5}$) changes from 0.1 M to 0.2 M, the pH of the solution

(a) increases by 1 unit (b) decreases by 1 unit
(c) remains same (d) becomes two times

D10. pH of sodium salt of chloroacetic acid ($pK_a = 3.4$) is 8.2. The concentration of the salt is

(a) 0.001 M (b) 0.01 M
(c) 1.0 M (d) 0.1 M.

Passage III

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation:

$X_2(g) \rightleftharpoons 2X(g)$

The standard Gibbs energy, $\Delta_r G°$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β .Thus, $\beta_{equilibrium}$ is the number of moles of X formed (Given: R = 0.083 L bar K^{-1} mol^{-1})

Answer the following questions:

D11. The equilibrium constant K_p for this reaction at 298 K in terms of $\beta_{equilibrium}$ is

(a) $\frac{8\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$ (b) $\frac{8\beta^2_{equilibrium}}{4-\beta^2_{equilibrium}}$
(c) $\frac{4\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$ (d) $\frac{4\beta^2_{equilibrium}}{4-\beta^2_{equilibrium}}$

D12. The incorrect statement among the following, for this reaction, is

(a) decrease in the total pressure will result in formation of more moles of gaseous X
(b) at the start of the reaction dissociation of gaseous X_2 takes place spontaneousty.
(c) $\beta_{equilibrium} = 0.7$
(d) $K_c < 1$

Answers

Passage I	**D1.** (d)	**D2.** (a)	**D3.** (c)	**D4.** (b)	**D5.** (b)				
Passage II	**D6.** (a)	**D7.** (a)	**D8.** (c)	**D9.** (c)	**D10.** (d)	**Passage III**	**D11.** (b)	**D12.** (c)	

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Assertion Reason Type Questions

The questions given below consists of an Assertion and the Reason. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

(*b*) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.

(*c*) If assertion is CORRECT but reason is INCORRECT.

(*d*) If assertion is INCORRECT but reason is CORRECT.

(*e*) If both assertion and reason are INCORRECT.

I.

1. Assertion : pH of water increases with increases in temperature.
Reason : With increase in temperature, K_w of water increases.)

2. Assertion : pH of HCl solution is less than that of acetic acid of same concentration.
Reason : CH_3COOH gives less number of H^+ ions because it is a weak acid.

3. Assertion : CO_2 is a Lewis base.
Reason : It can accept a proton.

4. Assertion : Buffer solutions are those which resist change in pH value on the addition of a small amount of acid or a base to it.
Reason : Mixture of NH_4OH and NH_4Cl acts as basic buffer.

5. Assertion : For acidic buffer, if ratio of conjugate acid-base pair is changed by 10 times, pH changes by ± 1.
Reason : pH always increases or decreases by 1 unit.

6. Assertion : In 0.1 M HCl, $[H^+]$ is also equal to 0.1 M but in 0.1 M CH_3COOH, $[H^+]$ is not equal to 0.1 M.
Reason : HCl is completely ionized but CH_3COOH does not ionize completely.

7. Assertion : For basic solution $[OH^-] > [H^+]$.
Reason : For acid solution $[H^+] > [OH^-]$

8. Assertion : CH_3COOH and CH_3COO^- are acid-base pairs.
Reason : These differ by H^+

9. Assertion : OH^- can behave as amphoteric.
Reason : It can accept and donate H^+.

10. Assertion : $CaO + SO_3 \rightarrow CaSO_3$ in an acid base reaction
Reason : It is in accordance with Bronsted concept.

11. Assertion : In the dissociation of PCl_5 at constant pressure and temperature addition of helium at equilibrium increases the dissociation of PCl_5.
Reason : Helium removes Cl_2 from the field of action.

12. Assertion : For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.
Reason : Equilibrium constant is independent of temperature.

II.

1. Assertion : K_p is always greater than K_c.
Reason : The effect of pressure is greater on the rate of reaction than the effect of concentration.

2. Assertion : The equilibrium constant does not change on addition of catalyst.
Reason : Catalyst does not take part in a chemical reaction

3. Assertion : In the reaction : $SO_2Cl_2(g) \rightleftharpoons SO_2(g)$, the reaction shifts to backward direction on increasing pressure.
Reason : The increase in pressure at equilibrium shifts the reaction towards lesser number of moles.

4. Assertion : For a gaseous reaction :
$2B \longrightarrow A$, the equilibrium constant K_p is less than K_c.
Reason : K_p is related to K_c as $K_p = K_c (RT)^{\Delta n_g}$.

5. Assertion : Pressure has no effect on the equilibrium reaction :

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Reason : Equilibrium constant of gaseous reactions is independent of pressure.

6. Assertion : Equilibrium is dynamic in nature.
Reason : Equilibrium can be attained from either direction.

7. Assertion : A solution containing a mixture of acetic acid and sodium acetate maintains a constant value of pH on addition of small amounts of acid or alkali.
Reason : A solution containing mixture of acetic acid and sodium acetate acts as a buffer solution having pH around 4.75.

8. Assertion : The ionisation of hydrogen sulphide in water is low in the presence of hydrochloric acid.
Reason : Hydrogen sulphide is a weak acid.

Answers

I. **1.** (*d*) **2.** (*a*) **3.** (*c*) **4.** (*b*) **5.** (*c*) **6.** (*a*) **7.** (*c*) **8.** (*a*) **9.** (*a*) **10.** (*c*) **11.** (*e*) **12.** (*c*)

II. **1.** (*e*) **2.** (*c*) **3.** (*a*) **4.** (*a*) **5.** (*c*) **6.** (*b*) **7.** (*a*) **8.** (*c*)

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Matching Type Questions

1. Dilution processes of different aqueous solutions, with water, are given in List I. The effects of dilution of the solutions on $[H^+]$ are given in List II.

(Note: Degree of dissociation (α) of weak acid and weak base is << 1; degree of hydrolysis of salt <<1; $[H^+]$ represents the concentration of H^+ ions)

List-I	List-II
(P) (10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 60 mL	1. The value of $[H^+]$ does not change on dilution
(Q) (20 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 80 mL	2. The value of $[H^+]$ changes to half of its initial value on dilution
(R) (20 mL of 0.1 M HCl + 20 mL of 0.1 M ammonia solution) diluted to 80 mL	3. The value of $[H^+]$ changes to two times of its initial value on dilution
(S) 10 mL saturated solution of $Ni(OH)_2$ in equilibrium with excess solid $Ni(OH)_2$ is diluted to 20 mL (solid $Ni(OH)_2$ is still present after dilution).	4. The value of $[H^+]$ changes to $\frac{1}{\sqrt{2}}$ times of its initial value on dilution
	5. The value of $[H^+]$ changes to $\sqrt{2}$ times of its initial value on dilution

Match each process given in List-I with one or more effect(s) in List-II.

The correct option is

(*a*) P → 4; Q → 2; R → 3; S → 1

(*b*) P → 4; Q → 3; R → 2; S → 3

(*c*) P → 1; Q → 4; R → 5; S → 3

(*d*) P → 1; Q → 5; R → 4; S → 1

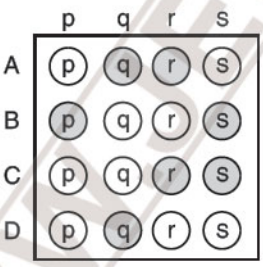
(JEE Advance 2018)

Answers

1. (*d*)

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.



If the correct matches are A-*q*, A-*r*, B-*p*, B-*s*, C-*r*, C-*s* and D-*q*, then the correctly bubbled matrix will look like the following:

1. Match the term given in Column I with the example in Column II.

Column I	Column II
(A) Bronsted base	(*p*) CN^-
(B) Lewis acid	(*q*) R—O—H
(C) Bronsted acid	(*r*) SiF_4
(D) Lewis base	(*s*) H_3PO_4

2. Match the description given in Column I with the reaction given in Column II.

Column I	Column II
(A) Reaction having $K_p < K_c$	(*p*) $2NO_2(g) \rightleftharpoons N_2O_4(g)$ ΔH = –ve
(B) Reaction in which equilibrium shifts towards right with increase in pressure	(*q*) $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$; ΔH = +ve
(C) Reaction in which equilibrium shifts towards right with increase in temperature	(*r*) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$; ΔH = +ve
(D) Reaction in which equilibrium does not shift by the addition of catalyst.	(*s*) $NH_4Cl(s) + (aq) + \text{heat} \rightarrow NH_4Cl(aq)$

Answers

1. : (A) – (*p*) (*q*) (B) – (*r*) (C) – (*s*) (D) – (*p*) (*q*)

2. : (A) – (*p*) (*q*) (B) – (*p*) (*q*) (C) – (*r*) (*s*) (D) – (*p*) (*q*) (*r*)

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3. Match the following species in Column I with the corresponding conjugate acid in Column II

Column I	Column II
(A) NH_3	(*p*) NH_4^+
(B) HCO_3^-	(*q*) H_3O^+
(C) H_2O	(*r*) H_2SO_4
(D) HSO_4^-	(*s*) H_2CO_3

Answers

3. : (A) – (*p*) (B) – (*s*) (C) – (*q*) (D) – (*r*)

Integer Type and Numerical Value Type Questions

Integer Type: The answer to each of the following question is a **single-digit**-integer ranging from 0 to 9.

1. Pressure necessary to obtain 50% dissociation of PCl_5 at 400 K is numerically.... times the value of equilibrium constant K_p.

2. In the reaction,
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
the molar concentrations of H_2, I_2, and HI are 0.1, 0.2 and 0.4 $molL^{-1}$ respectively at 700 K. The reaction quotient at this stage is

3. pOH of 1×10^{-5} M HCl solution is

4. One millilitre of 0.01 M HCl is added to 1L of NaCl solution. The pH of the resulting solution is

5. The pH of a 0.1 M solution of NH_4Cl is 5.127. The degree of hydrolysis is 7.46×10^{-n}. The value of *n* is

6. The pH of 10^{-2} M NaOH solution is *n* times the pH of 10^{-2} M HCl solution. The value of *n* is

7. pK_a of a weak acid is 5. pK_b of its conjugate base will be

8. 0.049 g of H_2SO_4 are present in 10L of solution. The pH of the solution is

9. A solution of pOH 3 is diluted 100 times. The pH of the resulting solution is

Numerical Value Type: Give the correct numerical value (in decimal notation truncated/rounded off to the second decimal place).

10. The solubility of a salt of weak acid (AB) at pH 3 is $Y \times 10^{-3}$ mol L^{-1}. The value of Y is.....
(Given that the value of solubility product of AB (K_{sp}) = 2×10^{-10} and the value of ionization constant of HB (K_a) = 1×10^{-8}.

Answers

1. (3) **2.** (8) **3.** (9) **4.** (5) **5.** (5) **6.** (6) **7.** (9) **8.** (4) **9.** (9) **10.** (4.47)

NCERT Exemplar Problems

Objective Questions

1. We know that the relationship between K_c and K_p is
$$K_p = K_c(RT)^{\Delta n_g}$$
What would be the value of Δn for the reaction
$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$
(*a*) 1 (*b*) 0.5
(*c*) 1.5 (*d*) 2

2. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the standard free energy is $\Delta G^\circ > 0$. The equilibrium constant (K) would be
(*a*) K = 0 (*b*) K > 1
(*c*) K = 1 (*d*) K < 1

3. Which of the following is not a general characteristic of equilibria involving physical processes ?
(*a*) Equilibrium is possible only in a closed system at a given temperature.
(*b*) All measurable properties of the system remain constant.
(*c*) All the physical processes stop at equilibrium.
(*d*) The opposing processes occur at the same rate and there is dynamic but stable condition.

Answers

1. (*d*) **2.** (*d*) **3.** (*c*)

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4. PCl_5, PCl_3 and Cl_2 are at equilibrium at 500K in a closed container and their concentrations are 0.8×10^{-3} mol L^{-1}, 1.2×10^{-3} mol L^{-1} respectively. The value of K_c for the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ will be
(*a*) 1.8×10^3 mol L^{-1} (*b*) 1.8×10^{-3}
(*c*) 1.8×10^{-3} L mol^{-1} (*d*) 0.55×10^4

5. Which of the following statements is incorrect ?
(*a*) In equilibrium mixture of ice and water kept in perfectly insulated flask mass of ice and water does not change with time.
(*b*) The intensity of red colour increases when oxalic acid is added to a solution containing iron (III) nitrate and potassium thiocyanate.
(*c*) On addition of catalyst the equilibrium constant value is not affected.
(*d*) Equilibrium constant for a reaction with negative ΔH value decreases as the temperature increases.

6. When hydrochloric acid is added to cobalt nitrate solution at room temperature, the following reaction takes place and the reaction mixture becomes blue. On cooling the mixture it becomes pink. On the basis of this information mark the correct answer.

$$[Co(H_2O)_6]^{3+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$$
(pink) (blue)

(*a*) $\Delta H > 0$ for the reaction
(*b*) $\Delta H < 0$ for the reaction
(*c*) $\Delta H = 0$ for the reaction
(*d*) The sign of ΔH cannot be predicted on the basis of this information.

7. The pH of neutral water at 25°C is 7.0. As the temperature increases, ionisation of water increases, however, the concentration of H^+ ions and OH^- ions are equal. What will be the pH of pure water at 60°C ?
(*a*) Equal to 7.0 (*b*) Greater than 7.0
(*c*) Less than 7.0 (*d*) Equal to zero

8. The ionisation constant of an acid, K_a, is the measure of strength of an acid. The K_a values of acetic acid, hypochlorous acid and formic acid are 1.74×10^{-5}, 3.0×10^{-8} and 1.8×10^{-4} respectively. Which of the following orders of pH of 0.1 mol dm^{-3} solutions of these acids is correct ?
(*a*) acetic acid > hypochlorous acid > formic acid
(*b*) hypochlorous acid > acetic acid > formic acid
(*c*) formic acid > hypochlorous acid > acetic acid
(*d*) formic acid > acetic acid > hypochlorous acid

9. K_{a_1}, K_{a_2} and K_{a_3} are the respective ionisation constants for the following reactions.

$$H_2S \rightleftharpoons H^+ + HS^-$$
$$HS^- \rightleftharpoons H^+ + S^{2-}$$
$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

The correct relationship between K_{a_1}, K_{a_2} and K_{a_3} is
(*a*) $K_{a_3} = K_{a_1} \times K_{a_2}$ (*b*) $K_{a_3} = K_{a_1} + K_{a_2}$
(*c*) $K_{a_3} = K_{a_1} - K_{a_2}$ (*d*) $K_{a_3} = K_{a_1} / K_{a_2}$

10. Acidity of BF_3 can be explained on the basis of which of the following concepts ?
(*a*) Arrhenius concept
(*b*) Bronsted Lowry concept
(*c*) Lewis concept
(*d*) Bronsted Lowry as well as Lewis concept.

11. Which of the following will produce a buffer solution when mixed in equal volumes ?
(*a*) 0.1 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl
(*b*) 0.05 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl
(*c*) 0.1 mol dm^{-3} NH_4OH and 0.05 mol dm^{-3} HCl
(*d*) 0.1 mol dm^{-3} CH_3COONa and 0.1 mol dm^{-3} NaOH

12. In which of the following solvent is silver chloride most soluble ?
(*a*) 0.1 mol dm^{-3} $AgNO_3$ solution
(*b*) 0.1 mol dm^{-3} HCl solution
(*c*) H_2O
(*d*) Aqueous ammonia

13. What will be the value of pH of 0.01 mol dm^{-3} CH_3COOH ($K_a = 1.74 \times 10^{-5}$) ?
(*a*) 3.4 (*b*) 3.6
(*c*) 3.9 (*d*) 3.0

14. K_a for CH_3COOH is 1.8×10^{-5} and K_b for NH_4OH is 1.8×10^{-5}. The pH of ammonium acetate will be
(*a*) 7.005 (*b*) 4.75
(*c*) 7.0 (*d*) Between 6 and 7

15. Which of the following options will be correct for the stage of half completion of the reaction $A \rightleftharpoons B$.
(*a*) $\Delta G^\circ = 0$ (*b*) $\Delta G^\circ > 0$
(*c*) $\Delta G^\circ < 0$ (*d*) $\Delta G^\circ = -RT \ln 2$

16. On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le Chatelier's principle. Consider the reaction :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature ?
(*a*) K will remain same
(*b*) K will decrease
(*c*) K will increase
(*d*) K will increase initially and decrease when pressure is very high

Answers

4. (*b*) **5.** (*b*) **6.** (*a*) **7.** (*a*) **8.** (*d*) **9.** (*a*) **10.** (*c*) **11.** (*c*) **12.** (*d*) **13.** (*a*) **14.** (*c*) **15.** (*a*) **16.** (*a*)

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17. What will be the correct order of vapour pressure of water, acetone and ether at 30°C. Given that among these compounds, water has maximum boiling point and ether has minimum boiling point ?

(*a*) Water < ether < acetone

(*b*) Water < acetone < ether

(*c*) Ether < acetone < water

(*d*) Acetone < ether < water

18. At 500 K, equilibrium constant, K_c, for the following reaction is 5.

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

What would be the equilibrium constant K_c for the reaction

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

(*a*) 0.04 (*b*) 0.4

(*c*) 25 (*d*) 2.5

19. In which of the following reactions, the equilibrium remains unaffected on addition of small amount of argon at constant volume ?

(*a*) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(*b*) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(*c*) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(*d*) The equilibrium will remain unaffected in all the three cases.

Answers

17. (*b*) **18.** (*a*) **19.** (*d*)

Multiple Choice Questions (Type-II)

20. For the reaction : $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the value of K is 50 at 400 K and 1700 at 500K. Which of the following options is correct ?

(*a*) The reaction is endothermic

(*b*) The reaction is exothermic

(*c*) If $NO_2(g)$ and $N_2O_4(g)$ are mixed at 400 K at partial pressures 20 bar and 2 bar respectively, more $N_2O_4(g)$ will be formed.

(*d*) The entropy of the system increases.

21. At a particular temperature and atmospheric pressure, the solid and liquid phases of a pure substance can exist in equilibrium. Which of the following term defines this temperature ?

(*a*) Normal melting point

(*b*) Equilibrium temperature

(*c*) Boiling point

(*d*) Freezing point

Answers

20. (*a*, *c*, *d*) **21.** (*a*, *d*)

Matching Type Questions

22. Match the following equilibria with the corresponding condition

(*i*) Liquid $\rightleftharpoons$ Vapour	(*a*) Saturated solution
(*ii*) Solid $\rightleftharpoons$ Liquid	(*b*) Boiling point
(*iii*) Solid $\rightleftharpoons$ Vapour	(*c*) Sublimation point
(*iv*) Solute (*s*) $\rightleftharpoons$ Solute (solution)	(*d*) Melting point

23. For the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Equilibrium constant $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

Some reactions are written below in Column I and their equilibrium constants in terms of K_c are written in Column II. Match the following reactions with the corresponding equilibrium constant.

Column I (Reaction)	***Column II (Equilibrium constant)***
(*i*) $2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$	(*a*) $2K_c$
(*ii*) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$	(*b*) $K_c^{1/2}$
(*iii*) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$	(*c*) $\frac{1}{K_c}$
	(*d*) K_c^2

Answers

22. (*i*) – (*b*); (*ii*) – (*d*); (*iii*) – (*c*); (*iv*) – (*a*), **23.** (*i*) – (*d*); (*ii*) – (*c*); (*iii*) – (*b*)

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24. Match standard free energy of the reaction with the corresponding equilibrium constant

(*i*) $\Delta G^\circ > 0$	(*a*) $K > 1$
(*ii*) $\Delta G^\circ < 0$	(*b*) $K = 1$
(*iii*) $\Delta G^\circ = 0$	(*c*) $K = 0$
	(*d*) $K < 1$

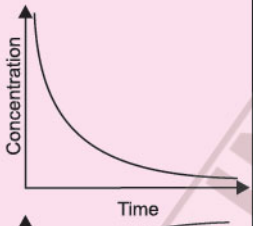
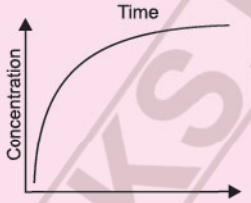
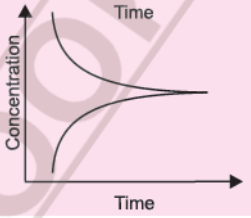
25. Match the following species with the corresponding conjugate acid

Species	*Conjugate acid*
(*i*) NH_3	(*a*) CO_3^{2-}
(*ii*) HCO_3^-	(*b*) NH_4^+
(*iii*) H_2O	(*c*) H_3O^+
(*iv*) HSO_4^-	(*d*) H_2SO_4
	(*e*) H_2CO_3

26. Match Column I with Column II.

Column I	*Column II*
(*i*) Equilibrium	(*a*) $\Delta G > 0, K < 1$
(*ii*) Spontaneous reaction	(*b*) $\Delta G = 0$
(*iii*) Non-spontaneous reaction	(*c*) $\Delta G^\circ = 0$
	(*d*) $\Delta G < 0, K > 1$

27. Match the following graphical variation with their description

A	*B*
(*i*) 	(*a*) Variation in product concentration with time
(*ii*) 	(*b*) Reaction at equilibrium
(*iii*) 	(*c*) Variation in reactant concentration with time

Answers

24. (*i*) – (*d*); (*ii*) – (*a*); (*iii*) – (*b*), **25.** (*i*) – (*b*); (*ii*) – (*e*); (*iii*) – (*c*); (*iv*) – (*d*)
26. (*i*) – (*b*, *c*); (*ii*) – (*d*); (*iii*) – (*a*) **27.** (*i*) – (*c*); (*ii*) – (*a*); (*iii*) – (*b*)

Assertion and Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

(*a*) Both A and R are true and R is the correct explanation of A.
(*b*) Both A and R are true but R is not the correct explanation of A.
(*c*) A is true but R is false.
(*d*) Both A and R are false.

28. Assertion (A) : Increasing order of acidity of hydrogen halides is HF < HCl < HBr < HI.

Reason (R) : While comparing acids formed by the elements belonging to the same group of periodic table, H–A bond strength is a more important factor in determining acidity of an acid than the polar nature of the bond.

29. Assertion (A) : A solution containing a mixture of acetic acid and sodium acetate maintains a constant value of pH on addition of small amounts of acid or alkali.

Reason (R) : A solution containing mixture of acetic acid and sodium acetate acts as a buffer solution around pH 4.75.

30. Assertion (A) : The ionisation of hydrogen sulphide in water is low in the presence of hydrochloric acid.

Reason (R) : Hydrogen sulphide is a weak acid.

31. Assertion (A) : For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.

Reason (R) : Equilibrium constant is independent of temperature.

32. Assertion (A) : Aqueous solution of ammonium carbonate is basic.

Reason (R) : Acidic/basic nature of a salt of weak acid and weak base depends on K_a and K_b value of the acid and the base forming it.

33. Assertion (A) : An aqueous solution of ammonium acetate can act as a buffer.

Reason (R) : Acetic acid is a weak acid and NH_4OH is a weak base.

34. Assertion (A) : In the dissociation of PCl_5 at constant pressure and temperature addition of helium at equilibrium increases the dissociation of PCl_5.

Reason (R) : Helium removes Cl_2 from the field of action.

Answers

28. (*a*) **29.** (*a*) **30.** (*b*) **31.** (*c*) **32.** (*a*) **33.** (*c*) **34.** (*d*)

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Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A1. (*b*) : Increase in temperature favours endothermic process.

A3. (*a*) : Decrease in temperature will favour backward (endothermic) reaction. Therefore, the forward reaction is exothermic *i.e.* $\Delta H > 0$ for the reaction.

A5. (*d*) :

	$PCl_5 \rightleftharpoons$	PCl_3	+ Cl_2
Initial conc.	1	0	0
At equ.	1–α	α	α

Total = 1– α + α + α = 1 + α

$$p(PCl_3) = \frac{\alpha}{1+a}.P$$

$$p(Cl_2) = \frac{\alpha}{1+a}.P$$

$$\therefore \quad K_p = \frac{p(PCl_3)\times p(Cl_2)}{p(PCl_5)}$$

$$= \frac{\left(\frac{\alpha}{1+\alpha}.P\right)\left(\frac{\alpha}{1+\alpha}.P\right)}{\frac{1-\alpha}{1-\alpha}.P} = \frac{\alpha^2 P}{1-\alpha^2}$$

A6. (*c*) : Forward rection will be favoured by increasing T.

A7. (*c*) : $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(aq)$ At equilibrium $p_{H_2} = 1.20$ atm and p_{CO_2} will also be 1.20 atm because originally equal number of moles of CO_2 and H_2 were taken.

Let $p_{CO} = p_{H_2O} = x$

$$\therefore \quad K_p = \frac{p_{CO}\times p_{H_2O}}{p_{CO_2}\times p_{H_2}} = 16$$

$$\frac{x\times x}{1.20\times 1.20}\times 16 \quad \text{or} \quad x^2 = 23.04$$

$$\therefore \quad x = 4.80 \text{ atm}$$

A8. (*c*) :

$$[H_2S] = \frac{1}{2} = 0.5 \text{ mol } L^{-1},$$

$$[H_2] = \frac{0.2}{2} = 0.1 \text{ mol } L^{-1}$$

$$[S_2] = \frac{0.8}{2} = 0.4$$

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2}$$

$$= \frac{(0.1)^2\times(0.4)}{(0.5)^2} = 0.016$$

A9. (*d*) : $A(s) \rightleftharpoons 2B(g) + 3C(g)$

Let x and y be the concentrations of B and C at equilibrium.

$K_c = x^2y^3$ ...(*i*)

Now, it concentration of C is changed to y' such that $y' = 2y$

If x' is the new conc. of B, then

$K_c = (x')^2(y')^3 = (x')^2(2y)^3$ ...(*ii*)

From (*i*) and (*ii*)

$(x')^2 8y^3 = x^2y^3$

$$(x')^2 = \frac{x^2}{8}$$

or $$x' = \sqrt{\frac{x^2}{8}} = \frac{x}{\sqrt[2]{2}}$$

i.e., $\frac{1}{\sqrt[2]{2}}$ times the original value.

A11. (*a*) : $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2 + 2H_2O$

$$K_p = \frac{P_{CO_2}}{p_{CH_4}[p_{O_2}]^2}$$

A13. (*d*) : $\Delta n_g = 1 - (1 + 3) = -2$

$K_p = 1.44 \times 10^{-5}$

$K_p = K_c(RT)^{\Delta n_g}$

or $$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{1.44\times10^{-5}}{(0.082\times777)^{-2}}$$

$$= 1.44 \times 10^{-5} / (0.082 \times 773)^{-2}$$

A14. (*c*) :

$$K_c = K_c(RT)^{\Delta n_g}$$

$$\Delta n_g = 1 - (1 + 1) = -1$$

$$\frac{K_p}{K_c} = (RT)^{-1} = \frac{1}{RT}$$

A15. (*d*) : $H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$

If the degree of dissociation is α

Initial conc.	1	0	0
At equiv	1–α	α	α/2

Total no. of moles at equilibrium = 1 – α + α + α/2 = 1 + α/2

$$p(H_2O) = \frac{1-\alpha}{1+\alpha/2}.P$$

$$p(H_2) = \frac{\alpha}{1+\alpha/2}.P$$

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$$p(O_2) = \frac{\alpha/2}{1+\alpha/2} . P$$

$$K_p = \frac{(p_{H_2})(p_{O_2})^{1/2}}{(p_{H_2O})} = \frac{\left(\frac{\alpha}{1+\alpha/2}P\right)\left(\frac{\alpha/2}{1+\alpha/2}P\right)^{1/2}}{\frac{1-\alpha}{1+\alpha/2}p}$$

$$= \frac{\left(\frac{2\alpha}{2+\alpha}P\right)\left(\frac{\alpha}{2+\alpha}P\right)^{1/2}}{\frac{2(1-\alpha)}{2+\alpha}P} = \frac{\alpha^{3/2}P^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$$

A16. (*b*) :

$$N_2O_4 \rightleftharpoons 2NO_2$$

Initial conc. 1.0 0

At equ. 1–0.20 0.40 mol

= 0.80 mol

Total moles = 0.80 + 0.40 = 1.20 mol

1 mol of vapour has pressure = 1 atm at 300 K

Applying $pV = nRT$

$1 \times V = 1 \times R \times 300$ ...(*i*)

When n = 1.2 mol, T = 600 K

$p \times V = 1.2 \times R \times 600$ ...(*ii*)

Dividing (*ii*) by (*i*)

p = 2.4 atm.

A17. (*d*) :

$$N_2O_4 \rightleftharpoons 2NO_2$$

Initial conc. 1 0

Let α is the degree of dissociation of N_2O_4.

Conc. at equ. $1-\alpha$ 2α

Total moles = $1 - \alpha + 2\alpha = 1 + \alpha$

$$p_{N_2O_4} = \frac{1-\alpha}{1+\alpha} . P$$

$$p_{NO_2} = \frac{2\alpha}{1+\alpha} . P$$

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}}$$

$$= \frac{\left(\frac{2\alpha}{1+\alpha}.P\right)^2}{\frac{1-\alpha}{1+\alpha}.P}$$

$$= \frac{4\alpha^2.P}{(1+\alpha)(1-\alpha)} = \frac{4\alpha^2.P}{1-\alpha^2}.$$

A18. (*c*) : pH will increase and solution will become less acidic.

A19. (*b*) : Resulting solution will be basic and therefore, will turn phenolphthalein solution pink.

A21. (*b*) :

$$[H^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{10^{-5}} = 10^{-9}\,M$$

$$pH = -\log [H^+] = -\log (10^{-9}) = 9.$$

A22. (*c*) : HSO_4^- can accept H^+ (H_2SO_4) as well as donate proton (SO_4^{2-}).

A23. (*b*) :

$$[H^+] = 0.05 \times 2 = 0.1 \text{ or } 1.0 \times 10^{-1}$$

$$pH = -\log 10^{-1} = 1.$$

A24. (*a*) : On heating water, its degree of ionization increases producing larger concentration of H_3O^+ and OH^- ions. Therefore, pOH will decrease.

A25. (*c*) :

$$K_{sp} \text{ of MOH} = 1 \times 10^{-10}$$

$$[M^+][OH^-] = 1 \times 10^{-10}$$

Now, $[M^+] = [OH^-]$

$\therefore$ $[OH^-]^2 = 1 \times 10–10$ or $[OH^-] = 10^{-5}$

$$[H_3O^+] = \frac{10^{-14}}{10^{-5}} = 10^{-9}$$

$$pH = -\log (10^{-9}) = 9.$$

A26. (*c*) : The resulting solution will be basic and therefore, pH will be greater than 7.

A27. (*b*) : *p*OH of 10^{-8} N NaOH is about 6.96.

A28. (*c*) : 50 mL of 0.4 M HCl = $\frac{0.4}{1000} \times 50$

= 0.02 g mol.

50 mL of 0.2 M NaOH = $\frac{0.2}{1000} \times 50$

= 0.01 g mol.

0.01 g mol of NaOH will neutralise 0.01 g mol of HCl

HCl left unneutralised = 0.01 g mol.

Vol. of solution = 50 + 50 = 100 mL

$$[HCl] = \frac{0.01}{100} \times 1000 = 0.1\ M$$

$[H^+]$ = 0.1 M

pH = – log (0.1) = 1.0

A29. (*a*) : $[H^+]_{HCl} = 10^{-8}$M

$[H^+]_{total} = [H^+]_{HCl} + [H^+]_{water}$

Let on ionization of water,

$[H^+] = [OH^-] = x$

$\therefore$ $[H^+]_{total} = 10^{-8} + x$

Now, $[H^+][OH^-] = 10^{-14}$

$(10^{-8} + x)(x) = 10^{-14}$

$x^2 = 10^{-8}x - 10^{-14} = 0$

Solving $x = 9.5 \times 10^{-8}$

$\therefore$ $[H^+]_{total} = 1 \times 10^{-8} + 9.5 \times 10^{-8}$

$= 10.5 \times 10^{-8}$M or $= 1.05 \times 10^{-7}$ M

A31. (*c*) : It will be acidic buffer having pH less than 7.

A32. (*b*) :

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

$$= 5 + \log \frac{(0.01)}{0.1} = 5 - 1 = 4$$

pH = 14 – pOH = 14 – 4 = 10.

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A33. (*d*) : The resulting solution will be basic and hence pH > 7.

A34. (*d*) : HNO_2 and $NaNO_2$ is acidic buffer (weak acid + salt of weak acid)

A35. (*c*) : Let solubility of $CaSO_4$ is x

$$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$$
$$x \quad x$$
$$K_{sp} = [Ca^{2+}][SO_4^{2-}] = x^2$$
$$\therefore \quad x^2 = 6.4 \times 10^{-5}$$
$$x = 8 \times 10^{-3}$$

A36. (*a*) : $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$[CrO_4^{2-}] = 2 \times 10^{-4}$, $[Ag^+] = 4 \times 10^{-4}$

$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$

$= (4 \times 10^{-4})^2 \times (2 \times 10^{-4})$

$= 32 \times 10^{-12}$

A37. (*b*) : $K_{sp}(CaC_2O_4) = 2.5 \times 10^{-9}$

$K_{sp} = s^2 = 2.5 \times 10^{-9}$

$\therefore \quad s = 5 \times 10^{-5}$

Solubility of $CaC_2O_4 = 5 \times 10^{-5}$ mol L^{-1}

$= 5 \times 10^{-5} \times 128$ g L^{-1}

$= 6.40 \times 10^{-3}$ or $= 0.0064$ g L^{-1}

A41. (*d*) : $MX_4 \rightleftharpoons M^+ + 4X^-$

If solubility is s, then

$[M^+] = s[X^-] = 4s$

$K_{sp} = [M^+][X^-]^4$

$= (s) \times (4s)^4$

$= 256\, s^5$

$\therefore \quad s = (K_{sp}/256)^{1/5}$

B. *mcq from competitive examinations*

B1. (*a*) : $\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.0 \times 10^{-5}}{10^{-1}}} = 10^{-2}$

$\therefore$ Percentage of acid dissociated $= 10^{-2} \times 100 = 1\%$

B2. (*c*) : $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$

$K = [Fe^{3+}][OH^-]^3$

Activity of solid is unity.

Conc. of OH^- ion in the reaction is decreased by 1/4 times, then equilibrium concentration of Fe^{3+} will be increased by $(4)^3 = 64$ times in order to keep the value of K to be constant.

B3. (*b*) : $HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2 \qquad K_1 = 8.0$

or $2HI \rightleftharpoons H_2 + I_2 \qquad K_2 = 64.0$

or $H_2 + I_2 \rightleftharpoons 2HI \qquad K_3 = \frac{1}{64}$

B4. (*b*) : $N_1V_1 + N_2V_2 + N_3V_3 = N_4V_4$

Let the volume of each acid solution mixed be 1 L

$10^{-3} \times 1 + 10^{-4} \times 1 + 10^{-5} \times 1 = N_4 \times 3$

$10^{-3} + 10^{-4} + 10^{-5} = N_4 \times 3$

$N_4 \times 3 = 1.11 \times 10^{-3}$

$N_4 = \frac{1.11 \times 10^{-3}}{3} = 0.37 \times 10^{-3}$

$[H^+] = 3.7 \times 10^{-4}$ M

B6. (*c*) : $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$K_1 = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

$= 1.5 \times 10^{-5}$

$HCN \rightleftharpoons H^+ + CN^-$

$K_2 = \frac{[CN^-][H^+]}{[HCN]}$

$= 4.5 \times 10^{-10}$

$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$

$K = \frac{[HCN][CH_3COO^-]}{[CN^-][CH_3COOH]}$

$= \frac{K_1}{K_2} = \frac{1.5 \times 10^{-5}}{4.5 \times 10^{-10}} \approx 0.3 \times 10^5$

$K = 3 \times 10^4$

B7. (*d*) : $K_h = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1.77 \times 10^{-5}}$

$= 5.6 \times 10^{-10}$

B8. (*d*) : Moles of H^+ ions in 20 mL of 0.05 M HCl

$= \frac{0.05}{1000} \times 20 = 1 \times 10^{-3}$ mol

Moles of OH^- ion in 30 mL of 0.10 M $Ba(OH)_2$

$= 2 \times \frac{0.10}{1000} \times 30$

$= 6 \times 10^{-3}$ mol

Moles of OH^- ions left unneutralised

$= 6 \times 10^{-3} - 1 \times 10^{-3}$

$= 5 \times 10^{-3}$ mol

Total volume of solution,

$= 20 + 30 = 50$ mL

$\therefore \quad [OH^-] = \frac{5 \times 10^{-3}}{50} \times 1000 = 0.1$ M

B9. (*b*) : $PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$

$s \quad 2s$

$K_{sp} = (s)(2s)^2 = 4s^3$

$[I^-] = 2.6 \times 10^{-3}$ M $= 2s$

$\therefore \quad s = \frac{2.6 \times 10^{-3}}{2}$ M $= 1.3 \times 10^{-3}$ M

$K_{sp} = 4s^3 = 4 \times (1.3 \times 10^{-3}\text{M})^3$

$= 8.8 \times 10^{-9}\, M^3$

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B11. (*b*) : $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$c - x \quad x \quad x$

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

$0.2 \quad 0.2\ M \quad 0.2\ M$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$[CH_3COOH] = c - x = 0.1\ M$

$[CH_3COO^-] = 0.2 + x = 0.2\ M$

$$\therefore \quad [H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]} = \frac{1.8\times10^{-5}\times0.1}{0.2}$$

$[H^+] = 9.0 \times 10^{-6}$

B12. (*b*) : $K_p = K_c (RT)^{\Delta n_g}$

$2C(s) + O_2(g) \rightleftharpoons 2CO(g)$

$\Delta n_g = 2 - 1 = 1$ for the reaction

Thus $K_p \neq K_c$

When $\Delta n_g = 0$, $K_p = K_c$ in options (*a*), (*c*) and (*d*).

B13. (*b*) : $pOH = pK_b + \log\frac{[B^-]}{[HB]}$

$pK_b = -\log K_b = -(\log 10^{-10}) = 10$

$\therefore \quad pOH = 10$

($\because$ concentration of $[B^-] = [HB]$)

$\therefore \quad pH = 14 - 10 = 4$

B15. (*b*) : $K_p = \frac{(p_{CO})^2}{p_{CO_2}}$ or $63 = \frac{(10\,p_{CO_2})^2}{p_{CO_2}}$

$\therefore \quad 63 = 100\,p_{CO_2}$ or $p_{CO_2} = 0.63$

$p_{CO} = 10 \times 0.63 = 6.3$

$p_{Total} = p_{CO_2} + p_{CO}$

$= 0.63 + 6.3 = 6.93$ atm.

B16. (*e*) : $K_p = \frac{\alpha^2 p}{1-\alpha^2}$ or $\frac{\alpha^2}{1-\alpha} = 2.56 \times 10^{-2}$

or $\alpha^2 = 2.56 \times 10^{-2} \quad (1 - \alpha \approx 1)$

$\therefore \quad \alpha = 0.16$, % dissociation = 16%

B18. (*d*) : Here $\Delta H < 0$ and $\Delta n < 0$

So, this will be favoured in the forward direction by high pressure and low temperature.

B19. (*b*) : $pOH = pK_b + \frac{[Salt]}{[Base]}$

$pK_b = -\log K_b = -\log(1.8 \times 10^{-5}) = 4.74$

$pOH = 4.74 + \log\left(\frac{0.20}{0.30}\right) = 4.56$

$pH = 14 - 4.56 = 9.44$

B20. (*c*) : $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad K_1$

$2NO(g) + O_2(g) \rightleftharpoons 2NO(g) \quad K_2$

Adding $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g) \quad K = K_1 \times K_2$

For $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)\ K' = \frac{1}{K_1K_2}$

or $NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g)\ K = \left(\frac{1}{K_1K_2}\right)^{1/2}$

B21. (*b*) : AB is a salt of weak acid and weak base.

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

$pK_a = 4.77,\ pK_b = 4.75$

$$\therefore \quad pH = 7 + \frac{1}{2} \times 4.77 - \frac{1}{2} \times 4.75 = 7.01$$

B22. (*d*) : For 0.01 M HCl, $pH = -\log 10^{-2} = 2$

For (*a*): $N_1V_1 + N_2V_2 = N_3(V_1 + V_2)$

$50 \times 0.01 + 50 \times 0.01 = N_3(100)$

$$N_3 = \frac{0.5 + 0.5}{100} = 10^{-2}$$

$pH = -\log(10^{-2}) = 2$ (No change in pH)

For (*b*): $50 \times 0.01 + 50 \times 0.002 = N_3 \times 100$

or $N_3 = \frac{0.5 + 0.1}{100} = 6 \times 10^{-3}$

$pH = -\log(6 \times 10^{-3}) = 2.22$ (pH increased)

For (*c*): $50 \times 0.01 + 150 \times 0.002 = N_3 \times 200$

or $N_3 = \frac{0.5 + 0.3}{200} = 4 \times 10^{-3}$

$pH = -\log(4 \times 10^{-3}) = 2.39$ (pH increased)

For (*d*): $50 \times 0.01 + 5 \times 1 = N_3 \times 55$

or $N_3 = \frac{0.5 + 5}{55} = 0.1$

$pH = -\log(10^{-1}) = 1$ (pH decreased)

B23. (*b*) : pH = 12, pOH = 2

$\therefore \quad [OH^-] = 10^{-2}$

$Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^-$

$K_{sp} = [Ba^{2+}][OH^-]^2$

If $[OH^-] = 10^{-2}$

Then, $[Ba^{2+}] = \frac{10^{-2}}{2}$

$$K_{sp} = \left(\frac{10^{-2}}{2}\right) \times (10^{-2})^2 = 5 \times 10^{-7}$$

B24. (*a*) : BF_3 is electron pair acceptor and hence Lewis acid.

B25. (*d*) : $pH = 10.97$

$-\log[H^+] = 10.97$

or $\log[H^+] = -10.97$

$[H^+] = \text{antilog}(-10.97)$

$= 1.06 \times 10^{-11}$

$$[OH^-] = \frac{1\times10^{-14}}{1.06\times10^{-11}} = 9.4 \times 10^{-4}\ M$$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

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$$K_b = \frac{[OH^-]^2}{[NH_3]}$$

$$= \frac{(9.4\times10^{-4})^2}{0.05} = 1.77\times10^{-5}$$

$$K_a \text{ (conjugate acid of } NH_3) = \frac{K_w}{K_b}$$

$$= \frac{1\times10^{-14}}{1.77\times10^{-5}} = 5.64\times10^{-10}$$

B26. (*a*) : BF_3 is electron pair acceptor and hence Lewis acid.

B27. (*b*) : $\Delta G = -2.303\ RT \log K$

$-172400 = -2.303\times8.314\times T\times\log(1\times10^{30})$

$$T = \frac{172400}{2.303\times8.314\times30}$$

or $T = 300\ K = 27°C$

B28. (*c*) : For the salt of weak acid (HA) and weak base (BOH):

$$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$$

$$= \frac{1}{2}(14.0 + 4.60 - 4.80)$$

$$= \frac{1}{2}\times 13.8 = 6.90$$

B29. (*a*) : $$\log\frac{K'_p}{K_p} = -\frac{\Delta H}{2.303}\left[\frac{1}{T_2}-\frac{1}{T_1}\right]$$

For an exothermic reaction, ΔH is –ve because heat is evolved. Therefore, T_2 is higher than T_1 so that $\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$ is –ve

so $\log K_p' - \log K_p$ = –ve or $\log K_p > \log K_p'$ or $K_p > K_p'$

B31. (*c*) : Hydrolysis of salts give different aqueous solutions as KCl (neutral), NaCl (neutral), Na_2CO_3 (basic) and $CuSO_4$ (acidic). Since aqueous solution of Na_2CO_3 is basic, pH will be more than 7 while for KCl (pH = 7), NaCl (pH = 7) and $CuSO_4$ (pH < 7).

B32. (*b*) : For a sparingly soluble salt

$\Delta G = -2.303\ RT \log K_{sp}$

$63300 = -2.303\times8.314\times298\log K_{sp}$

or $\log K_{sp} = -11.093$

or $K_{sp} = 8\times10^{-12}$

B33. (*b*) : $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$$K_C = \frac{[NO]^2}{[N_2][O_2]}$$

$$K_C = \frac{(1.4\times10^{-3})^2}{(0.36\times10^{-3})(4.41\times10^{-3})}$$

$$= 1.234$$

$$NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$$

$$K_C' = \frac{1}{\sqrt{K_C}} = \frac{1}{\sqrt{1.234}} = 0.9$$

B35. (*b*) : The salt having highest solubility will be precipitated at the last.

$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$K_{sp} = (2s)^2(s) = 4s^3$

$$\therefore \quad s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.1\times10^{-12}}{4}} = 0.65\times10^{-4}$$

For AgCl, AgBr and AgI, solubility, $s = \sqrt{K_{sp}}$

For AgCl, $s = \sqrt{1.8\times10^{-10}} = 1.34\times10^{-5}$

For AgBr, $s = \sqrt{5.0\times10^{-13}} = 0.707\times10^{-6}$

For AgI = $s = \sqrt{8.3\times10^{-17}} = 0.91\times10^{-8}$

Thus, solubility of Ag_2CrO_4 is highest and it will be precipitated at the last.

B36. (*c*) : $NaOH + HCl \longrightarrow NaCl + H_2O$

When equal volumes of 0.01 M HCl and 0.1 M NaOH are mixed 0.01 M of HCl will react with 0.01 M NaOH for neutralisation.

Moles of NaOH left = 0.1 – 0.01 = 0.09 moles

Since volume becomes double on mixing,

$$[OH^-] = \frac{0.09}{2} = 0.045\ M$$

$pOH = -\log(OH^-)$

$= -\log(0.045) = 1.35$

$pH = 14 - 1.35 = 12.65$

B37. (*c*) : Acidic buffer is formed by weak acid and its salt. However, $HClO_4$ is a strong acid and therefore, $HClO_4$ and $NaClO_4$ donot form acidic buffer.

B40. (*d*) : For MY salt,

$MY \rightleftharpoons M^+ + Y^-$

If solubility of MY is *s*, then

$K_{sp} = s^2$

or $s = \sqrt{K_{sp}} = \sqrt{6.2\times10^{-13}} = 7.87\times10^{-7}$

For NY_3 salt,

$NY_3 \rightleftharpoons N^{3+} + 3Y^-$

If solubility of NY_3 is s'

$K_{sp} = s'\times(3s')^3 = 27s'^4$

$$\text{or } s' = \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}} = \left(\frac{6.2\times10^{-13}}{27}\right)^{\frac{1}{4}} = 3.85\times10^{-4}$$

$\therefore \quad s(MY) < s'(NY_3)$

B41. (*b*) : $C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$

$$\alpha = \sqrt{\frac{K_b}{c}} = \sqrt{\frac{1.7\times10^{-9}}{0.1}} = 1.30\times10^{-4}$$

Percentage of pyridine that forms pyridinium ion

$= 1.30\times10^{-4}\times100 = 0.013\%$

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B42. (*b*) : $AgCl\,(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

Let solubility of AgCl be *s*

$$NaCl\,(aq) = Na^+(aq) + Cl^-(aq)$$
$$0.1M \quad 0.1M$$
$$[Ag^+] = s, [Cl^-] = s + 0.1$$
$$K_{sp} = [Ag^+]\,[Cl^-]$$
$$1.6 \times 10^{-10} = s(s + 0.1)$$

Since solubility of AgCl is very small, then

$s << 0.1$

$\therefore 1.6 \times 10^{-10} = s\,(0.1)$

or $s = \dfrac{1.6\times10^{-10}}{0.1} = 1.6\times10^{-9}\ \text{molL}^{-1}$

B44. (*a*) : (*i*) $2NH_3 \rightleftharpoons N_2 + 3H_2$; $\dfrac{1}{K_1}$

(*ii*) $N_2 + O_2 \rightleftharpoons 2NO$; K_2

(*iii*) $3H_2 + \dfrac{3}{2}O_2 \rightleftharpoons 3H_2O$; K_3^3

By adding Eqns. (*i*), (*ii*) and (*iii*)

$$2NH_3 + \frac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2$$

$$K = \frac{K_2K_3^3}{K_1}$$

B45. (*d*) : Minimum pressure of CO_2 = Pressure of CO_2 at equilibrium.

$$SrCO_3\,(s) \rightleftharpoons SrO(s) + CO_2(g)$$

$K_p = p(CO_2) = 1.6$ atm

Maximum pressure of CO_2 = 1.6 atm

$p_1V_1 = p_2V_2$ (n, T constant)

$0.4 \times 20 = 1.6 \times V_2$

$$V_2 = \frac{0.4\times20}{1.6} = \mathbf{5\ L}$$

B46. (*c*) : $Ag_2C_2O_4(s) \rightleftharpoons 2Ag^+(aq) + C_2O_4^{2-}(aq)$

1 0 0

$(1-s)$ $2s$ s

$[Ag^+] = 2s = 2.2 \times 10^{-4}$ mol L^{-1}

$$[C_2O_4^{2-}] = s = \frac{2.2\times10^{-4}}{2} = 1.1 \times 10^{-4}\ \text{mol L}^{-1}$$

$K_{sp} = [Ag^+]^2\,[C_2O_4^{2-}]$

$= (2.2 \times 10^{-4})^2 = (1.1 \times 10^{-4})$

$= \mathbf{5.324 \times 10^{-12}}$

B47. (*a*) : The reaction is exothermic, low temperature will favour the reaction.

$\Delta n_g = 1 - (1 + 1) = -1 = -ve$

High pressure will favour the reaction.

B48. (*a*) : Solubility of $BaSO_4 = 2.4 \times 10^{-3}\ gL^{-1}$

$$\frac{2.4\times10^{-3}}{233} = 1.038\times10^{-5}\ \text{mol L}^{-1}$$

$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$

$K_{sp} = [Ba^{2+}][SO_4^{2-}]$

$= (1.038 \times 10^{-5}) \times (1.038 \times 10^{-5})$

$= 1.08 \times 10^{-10}\ \text{mol}^2\ L^{-2}$

B49. (*d*) : Moles of HCl $= \dfrac{1}{5}\times\dfrac{75}{1000} = 15\times10^{-3}$

Moles of NaOH $= \dfrac{1}{5}\times\dfrac{25}{1000} = 5\times10^{-3}$

Moles of HCl in resulting solution

$= 15 \times 10^{-3} - 5 \times 10^{-3}$

$= 10 \times 10^{-3} = 1 \times 10^{-2}$

Volume of resulting solution

$= 75 + 25 = 100$ mL

Concentration of H^+ ions in solution

$$[H^+] = \frac{1\times10^{-2}}{100}\times1000$$
$$= 1 \times 10^{-1}$$
$$pH = -\log[H^+] = -\log(1 \times 10^{-1})$$
$$= 1$$

B50. (*d*) : $pH = -\log[H^+]$

or $[H^+]$ = Antilog $(-pH)$

= Antilog (-5.4)

$= 3.98 \times 10^{-6}$M

B51. (*d*) : Ionic product of $CaF_2 = [Ca^{2+}]\,[F^-]^2$

On mixing, concentrations of ions will be reduced to half

$$(a)\ \frac{10^{-2}}{2}\times\left(\frac{10^{-5}}{2}\right)^2 = \frac{1}{8}\times10^{-12}$$

$$(b)\ \frac{10^{-3}}{2}\times\left(\frac{10^{-3}}{2}\right)^2 = \frac{1}{8}\times10^{-9}$$

$$(c)\ \frac{10^{-4}}{2}\times\left(\frac{10^{-2}}{2}\right)^2 = \frac{1}{8}\times10^{-8}$$

$$(d)\ \frac{10^{-2}}{2}\times\left(\frac{10^{-3}}{2}\right)^2 = \frac{1}{8}\times10^{-8}$$

In 2, 3 and 4, ionic product is greater than K_{sp}. Hence precipitation will occur in 2,3 and 4.

B52. (*d*) : $SO_3\,(g) \rightleftharpoons SO_2(g) + 1/2O_2(g)$ $K_c = 4.9 \times 10^{-2}$

For the reaction,

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_c' = \frac{1}{K_c^2}$$
$$= \frac{1}{(4.9\times10^{-2})^2} = 416.49 \approx 416$$

B53. (*c*) : $$K = \frac{[NO]^2[O_2]}{[NO_2]^2} = 2 \times 10^{-6}$$

$$K' = \frac{[NO_2]^4}{[NO]^4[O_2]^2} = \frac{1}{(K)^2}$$
$$= \frac{1}{(2\times10^{-6})^2} = \frac{10^{12}}{4} = 2.5 \times 10^{11}.$$

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B54. (*a*) : $AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$

Let the solubility of $AgIO_3$ in a saturated solution = s

$K_{sp} = [Ag^+][IO_3^-] = s \times s = s^2$

$s = \sqrt{K_{sp}} = \sqrt{1.0\times10^{-8}} = 10^{-4}$ mol L^{-1}

Concentration = $10^{-4} \times 283$ g L^{-1}

or $= \dfrac{10^{-4}\times283\times100}{1000}$

$= 2.83 \times 10^{-3}$ g per 100 mL.

B55. (*b*) : $K_{overall} = K_{a_1} \times K_{a_2}$

$= 1 \times 10^{-5} \times 5 \times 10^{-10} = 5 \times 10^{-15}$.

B56. (*b*) : If the given weak acid is 50% ionized then its conjugate base will have the concentration same as that of weak acid.

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$= 4.5 + \log \frac{0.5\,c}{0.5\,c} = 4.5$$

$\therefore$ pOH = 14 – 4.5 = 9.5

B57. (*b*) : 30 mL of 1N HCl will neutralise 30 mL of 1 N NaOH. Therefore, 20 mL of 1 N HCl will be left unneutralized.

Volume of mixture = 50 + 30 = 80 mL

$$[HCl] = \frac{20}{80} = 0.25\,M$$

$[H^+]$ = 0.25 M

pH = $-\log[H^+] = 0.6021$

B58. (*d*) : $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$; K_1

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$; K_2

$CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$; K_3

$\therefore K_3 = K_1 \times K_2$

B59. (*d*) : $pH = \dfrac{1}{2}pK_w + \dfrac{1}{2}(pK_a - pK_b)$

$= 7 + \dfrac{1}{2}(4.8 - 4.78) = 7.01$

B60. (*b*) :

	$2SO_2(g)$	+ $O_2(g)$	$\longrightarrow$ $2SO_3(g)$
Initially	5 mol	5 mol	0 mol

Moles of SO_2 used up at equilibrium

$= 5 \times \dfrac{60}{100} = 3$ mol

At equilibrium moles of SO_2 left

= 5 – 3 = 2 mol

Moles of O_2 reacted = 1.5 mol

Moles of O_2 left = 3.5

Moles of SO_3 produced = 3 mol

Total number of moles

= 2 + 3.5 + 3 = 8.5 mol

Mole fraction of $O_2 = \dfrac{3.5}{8.5}$

$p_{O_2} = x_{O_2} \times p$

where total pressure, p = 1 atm

$p_{O_2} = \dfrac{3.5}{8.5} \times 1 = 0.41$ atm.

B61. (*a*) : Total moles of H^+

$= \dfrac{20\times1}{1000\times2} + \dfrac{30\times1}{1000\times3}$

$= 2.0 \times 10^{-2}$ mol

Total moles of OH^-

$= \dfrac{40}{1000} \times \dfrac{1}{4} = 1.0\times10^{-2}$ mol

Thus, moles of H^+ left

$= 2 \times 10^{-2} - 1.0 \times 10^{-2}$

$= 1 \times 10^{-2}$ mol

Total volume of solution

= $1dm^3$ = 1000 mL

$[H^+] = 10^{-2}$ M

pH = $-\log[H^+] = -\log 10^{-2} = 2$

B62. (*c*) : $K_{sp} = [Ba^{2+}][CO_3^{2-}]$

$5.1 \times 10^{-9} = [Ba^{2+}] \times 10^{-4}$

$[Ba^{2+}] = 5.1 \times 10^{-5}$ M

B63. (*b*) : Moles of HCl in 2mL of 0.1M solution

$= \dfrac{0.1}{1000} \times 2 = 2 \times 10^{-4}$ moles

Moles of H_2SO_4 in 2 mL of 0.1M solution

$= \dfrac{0.1}{1000} \times 2 = 2 \times 10^{-4}$ moles.

Total moles of H^+ = Moles of HCl + 2(Moles of H_2SO_4)

$= 2 \times 10^{-4} + (2 \times 2 \times 10^{-4})$

$= 6 \times 10^{-4}$ moles

Total volume = 6 mL

$[H^+] = \dfrac{6\times10^{-4}}{6} \times 1000 = 10^{-1}$ N

$\therefore$ pH = $-\log[H^+] = -\log 10^{-1} = 1$

B64. (*c*) : H^+ ion are given only by $HClO_4$ and not by $KClO_4$.

$\therefore [H^+] = [HClO_4] = 2 \times 10^{-3}$ M.

Since, equal volumes of $HClO_4$ and $KClO_4$ are mixed, the total volume becomes double, and the concentration becomes half of the previous value.

$\therefore$ Concentration $HClO_4$ after mixing with $KClO_4$ solution $= \dfrac{1}{2}(2 \times 10^{-3})\,M = 10^{-3}$ M

$\therefore [H^+] = 10^{-3}$ M

pH = $-\log[H^+] = -\log 10^{-3} = 3$

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B65. (*c*) : $2PQ \rightleftharpoons P_2 + Q_2$

$$K_1 = \frac{[P_2][Q_2]}{[PQ]^2} = 2.5 \times 10^5$$

$$PQ + \frac{1}{2}R_2 \rightleftharpoons PQR$$

$$K_2 = \frac{[PQR]}{[PQ][R_2]^{1/2}} = 5 \times 10^{-3}$$

$$\frac{1}{2}P_2 + \frac{1}{2}Q_2 + \frac{1}{2}R_2 \rightleftharpoons PQR$$

$$K_3 = \frac{[PQR]}{[P_2]^{1/2}[Q_2]^{1/2}[R_2]^{1/2}}$$

$$= \frac{K_2}{\sqrt{K_1}} = \frac{5\times10^{-3}}{\sqrt{2.5\times10^5}}$$

$$= 1 \times 10^{-5}$$

B66. (*a*) : $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-, K_1 = 4.2 \times 10^{-7}$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}, K_2 = 4.8 \times 10^{-11}$

Since $K_1 >> K_2$, conc. of H^+ and HCO_3^- are approximately equal.

B67. (*d*) : $Mg(OH)_2$ dissociates as :

$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}}$$

$$[OH^-] = \sqrt{\frac{1\times10^{-11}}{0.001}} = 1 \times 10^{-4}$$

$\therefore$ pOH = 4

pH = 14 – pOH = 10

B68. (*d*) : For AgBr, $K_{sp} = 5.0 \times 10^{-13}$

Precipitation of AgBr will occur when ionic product $[Ag^+][Br^-]$ becomes larger than K_{sp}

$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$

$$K_{sp} = [Ag^+][Br^-]$$

$$[Ag^+] = 0.05 \text{ M}$$

The concentration of Br^- required to start precipitation.

$$[Br^-] = \frac{K_{sp}}{[Ag^+]} = \frac{5.0\times10^{-13}}{0.05}$$

$$= 1.0 \times 10^{-11}$$

Now, $[Br^-] = [KBr]$

Molar mass of KBr = 120

$\therefore$ Amount of KBr required

$$= 1.0 \times 10^{-11} \times 120$$

$$= 1.20 \times 10^{-9} \text{ g}$$

B69. (*a*) :

$$K_1 = \frac{[SO_3]}{[SO_2][O_2]^{1/2}}$$

$$K_2 = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$$

$$K_2 = \frac{1}{K_1^2}$$

B70. (*d*) : $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$

If solubility is *y*

$[Ca^{2+}] = 3y, [PO_4^{3-}] = 2y$

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

$$= (3y)^3(2y)^2 = 108y^5.$$

B71. (*c*) :

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

Initial conc. c 0 0

At. equ. $c(1-\alpha)$ $cx\alpha$ $cy\alpha$

$$K_{eq} = \frac{(cx\alpha)^x(cy\alpha)^y}{c(1-\alpha)}$$

Assuming $(1-\alpha) \simeq 1$

$$K_{eq} = C^{x+y-1}.x^x.y^y\alpha^{x+y}$$

or $$\alpha^{x+y} = \frac{K_{eq}}{C^{x+y-1}.x^x.y^y}$$

$\therefore$ $$\alpha = \left[\frac{K_{eq}}{C^{x+y-1}.x^xy^y}\right]^{\frac{1}{x+y}}$$

B72. (*d*) : Ag_2CO_3 is most soluble (solubility = 1.26×10^{-4}) and AgI is least soluble (solubility = 1×10^{-8})

B73. (*a*) : $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Moles of PCl_5 dissociated = $4 \times \frac{50}{100} = 2$ mol

Concentration at equilibrium

$$[PCl_5] = \frac{2}{4}, [PCl_3] = \frac{2}{4}, [Cl_2] = \frac{2}{4}$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{2}{4}\times\frac{2}{4}}{\frac{2}{4}} = 0.5 \text{ mol L}^{-1}.$$

B74.(*a*) : CH_3COOH is a weak acid. It does not dissociate completely and therefore, its pH ≠ 1.

B75. (*d*) : Total moles of sodium acetate = 0.1 + 0.1 = 0.2

$$pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$pH = pK_a + \log\frac{0.2}{0.1} = pK_a + \log 2.$$

B76. (*b*) : Ionic product of ZnS = $[Zn^{2+}][S^{2-}]$

$$= 0.1 \times 8.1 \times 10^{-19} = 8.1 \times 10^{-20}$$

$K_{sp}(ZnS) = 3 \times 10^{-22}$

Since ionic product of ZnS is greater than K_{sp} precipitation will occur.

Ionic product of CuS = $[Cu^{2+}][S^{2-}]$

$$= 0.01 \times 8.1 \times 10^{-19} = 8.1 \times 10^{-21}$$

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$K_{sp}(CuS) = 8 \times 10^{-36}$

Ionic product of CuS > K_{sp}

∴Precipitation of CuS will also occur. So, both ZnS and CuS precipitate.

B77. (*a*) : $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

0.5 atm	0
(0.5 – *x*) atm	2*x* atm

Now, $0.5 - x + 2x = 0.8$ or $x = 0.3$ atm

$p_{CO} = 2 \times 0.3 = 0.6$ atm

$p_{CO_2} = 0.5 - 0.3 = 0.2$ atm

$$K_p = \frac{(p_{CO})^2}{p_{CO_2}} = \frac{0.6 \times 0.6}{0.2} = 1.8 \text{ atm.}$$

B78. (*b*) : Let *s* be the solubility of $Cr(OH)_3$

$$Cr(OH)_3 \rightleftharpoons Cr^{3+} + 3OH^-$$

$$s \quad 3s$$

$$K_{sp} = [Cr^{3+}][OH^-]^3 = (s)(3s)^3 = 27s^4$$

$$27s^4 = 1.6 \times 10^{-30}$$

$$\therefore \quad s = \sqrt[4]{1.6 \times 10^{-30}/27}.$$

B79. (*d*) : $pH = 5, [H^+] = 10^{-5}$ M

$$[H^+] = \sqrt{K_a \cdot C}$$

or $$K_a = \frac{[H^+]^2}{C} = \frac{(1 \times 10^{-5})^2}{1.0} = 1.0 \times 10^{-10}.$$

B80. (*c*) : Hydrolysis of a salt of weak acid and weak base :

$$pH = 7 + \frac{1}{2}(pK_a - pK_b)$$

Now $pK_a = pK_b$

∴ $pH = 7$

B81. (*a*) : $$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$$

$$K_{sp} = [Fe^{3+}][OH^-]^3$$

If *s* is the solubility, $[Fe^{3+}] = s, [OH^-] = 3s$

$$K_{sp} = (s)(3s)^3 = 27s^4$$

B82. (*b*) : $$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

$$pK_b = -\log K_b = -\log 10^{-9} = 9$$

∴ $pOH = 9 + 0 = 9$

or $pH = 14 - 9 = 5$

B83. (*b*) : For the reaction : $2A \rightarrow B + C$

$$\text{or} \quad K_c = \frac{[B][C]}{[A]^2}$$

$$= \frac{(2 \times 10^{-3})(3 \times 10^{-3})}{(10^{-3})^2} = 6$$

B84. (*c*) : For $pH = 3$, $[H_3O^+] = 10^{-3}$

For $pH = 4$, $[H_3O^+] = 10^{-4}$

Moles of H_3O^+ in 100 mL of solution of pH (= 3)

$$= \frac{10^{-3}}{1000} \times 100 = 10^{-4}$$

Moles of H_3O^+ in 400 mL of solution of pH (= 4)

$$= \frac{10^{-4}}{1000} \times 400 = 4 \times 10^{-5}$$

Total moles of H_3O^+ on mixing

$$= 10^{-4} + 4 \times 10^{-5} = 14 \times 10^{-5}$$

$$[H_3O^+] = \frac{14 \times 10^{-5} \times 1000}{500} = 2.8 \times 10^{-4}$$

$$pH = -\log(2.8 \times 10^{-4})$$

$$= 4 - \log 2.8$$

B85.(*b*) : Equivalents of OH^- in 5 mL of 0.4 N NaOH

$$= \frac{0.4}{1000} \times 5 = 2 \times 10^{-3}$$

Equivalents of H^+ in 20 mL of 0.1 N HCl

$$= \frac{0.1}{1000} \times 20 = 2 \times 10^{-3}$$

On mixing 2×10^{-3} equivalents of OH^- ions and 2×10^{-3} equivalents of H^+ ions, the solution will become neutral. Its pH will be 7.

B86.(*d*) : Equivalents of H^+ ions in 20mL of 0.1 N HCl

$$= \frac{0.1}{1000} \times 20 = 2 \times 10^{-3}$$

For pH = 1, $[H^+] = 10^{-1}$

Equivalents of H^+ ions in 500 mL = $\frac{10^{-1} \times 500}{1000}$

$$= 0.05 \text{ or } 5 \times 10^{-2}$$

Equivalents of H^+ ions on adding

$$= 2 \times 10^{-3} + 5 \times 10^{-2}$$

$$= 52 \times 10^{-3}$$

Volume of solution = 500 + 20 = 520

$$[H^+] = \frac{52 \times 10^{-3}}{520} \times 1000 = 0.1$$

$$pH = -\log(0.1) = 1$$

B87.(*a*) : $pH + pOH = 14$

or $pOH = 14 - pH$

$= 14 - 10.65 = 3.35$

$-\log[OH^-] = 3.35$

$\log[OH^-] = -3.35$

or $[OH^-] = 4.47 \times 10^{-4}$ M

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

Since 1 mol of $Ca(OH)_2$ gives 2 moles of OH^-

$$[Ca(OH)_2] = \frac{4.47 \times 10^{-4}}{2}$$

$$= 2.235 \times 10^{-4} \text{ M}$$

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Moles of $Ca(OH)_2$ to be dissolved in 250 mL

$$= \frac{2.235 \times 10^{-4} \times 250}{1000}$$

$$= 5.58 \times 10^{-5}$$

B88. (*c*) : $N_2(g) + O_2(g) \rightarrow 2NO(g)$; $K = 4 \times 10^{-4}$

Let equilibrium constant is K′ for the reaction,

$$NO(g) \rightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$$

$$K' = \frac{1}{\sqrt{K}} = \frac{1}{\sqrt{4 \times 10^{-4}}}$$

$$= \frac{1}{2 \times 10^{-2}} = 50$$

B89. (*b*) : If x is the degree of dissociation,

	HQ	$\rightleftharpoons$	H^+	+	Q^-
Initial conc.	0.1		0		0
After dissociation	$0.1 - x$		x		x

Now $pH = 3$, $[H^+] = 10^{-3}$ or $x = 10^{-3}$

$$K_a = \frac{x \times x}{0.1 - x} = \frac{(10^{-3})^2}{0.1 - 10^{-3}}$$

Assuming $0.1 - 10^{-3} \approx 0.1$

$$K_a = \frac{(10^{-3})^2}{0.1} = 1 \times 10^{-5}$$

B90. (*b*) : $CH_3COO^- + H^+ \longrightarrow CH_3COOH$

$$[CH_3COO^-] = 0.01 - 0.001 = 0.009 \text{ M}$$

$$[CH_3COOH] = 0.01 + 0.001 = 0.011 \text{ M}$$

$$pH = pK_a + \frac{[Salt]}{[Acid]}$$

$$= 4.75 + \log \frac{0.009}{0.011}$$

$$= 4.75 - 0.087 = 4.662$$

B92. (*d*) : $pOH = pK_b - \log \frac{[Base]}{[Salt]}$

$$14 - pH = pK_b - \log \frac{[Base]}{[Salt]}$$

$$14 = pH + pKb - \log \frac{[Base]}{[Salt]}$$

$$14 = 13 - \log \frac{[Base]}{[Salt]}$$

$$\therefore \quad \log \frac{[Base]}{[Salt]} = -1 \quad \text{or} \quad \frac{[Base]}{[Salt]} = 0.1$$

B93. (*d*) : $AB \rightleftharpoons A^+ + B^-$ .....K_1

$AB_2^- \rightleftharpoons AB + B^-$ ..... K_2

Adding

$$AB_2^- = A^+ + 2B^-$$

$$K = \frac{[A^+][B^-]^2}{[AB_2^-]}$$

$$\frac{[A^+]}{[AB_2^-]} = \frac{K}{[B^-]^2}$$

i.e., inversely proportional to $[B^-]^2$

B95. (*e*) : $pH = 12$

$\therefore$ $pOH = 14 - pH = 14 - 12 = 2$

$pOH = -\log[OH^-] = 2$

or $[OH^-] = 1 \times 10^{-2}$ M

$X(OH)_2 \rightleftharpoons X^{2+} + 2OH^-$

If $[OH^-] = 1 \times 10^{-2}$ M, then $[X^{2+}] = \frac{1}{2} \times 10^{-2}$ M

$$= 0.5 \times 10^{-2} \text{ M}$$

$K_{sp} = [X^{2+}][OH^-]^2 = (0.5 \times 10^{-2}) \times (1 \times 10^{-2})^2$

$= 5 \times 10^{-7}$ mol^3 L^{-3}

B96. (*c*) : For the reaction : $A_2(s) \rightleftharpoons B_2(s) + 2C(g)$

Moles of B $= \frac{1}{50}$

Moles of C $= \frac{1}{50} \times 2 = 0.04$ mol

Applying ideal gas equation,

$pV = nRT$

$p \times 24.6 = 0.04 \times 0.082 \times 300$

$$p = \frac{0.04 \times 0.082 \times 300}{24.6} = 0.04 \text{ atm}$$

$K_p = p_C^2 = (0.04)^2 = 1.6 \times 10^{-3}$ atm^2

B97. (*b*) : $pH = -\log [H^+]$

$= -\log (3.8 \times 10^{-3})$

$= -[(\log 3.8) + (\log 10^{-3})]$

$= -[0.58 + (-3)] = 2.42$

B98. (*c*) : Conc. of H^+ ions in 10 mL of 0.1 M H_2SO_4

$$= \frac{0.1}{1000} \times 10 \times 2 = 0.002 \text{ M}$$

Conc. of OH^- ions in 10 mL of 0.1 M KOH

$$= \frac{0.1}{1000} \times 10 = 0.001 \text{ M}$$

Conc. of H^+ ions left after mixing

$= 0.002 - 0.001 = 0.001$ M

or $= 10^{-3}$ M

$\therefore$ $pH = -\log [H^+] = -\log (10^{-3}) = 3.0$

B99. (*c*) : $Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$

$K_{sp} = [Ca^{2+}][OH^-]^2$

If solubility is s, then

$[Ca^{2+}] = s$, $OH^- = 2s$

$\therefore$ $K_{sp} = (s)(2s)^2 = 4s^3$

$$= 4 \times \left(\sqrt{3}\right)^3 = 12\sqrt{3}$$

B100. (*c*) : $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

$$\Delta n_g = 1 - (1 + \frac{1}{2}) = -\frac{1}{2}$$

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B101. (*a*) : $2SO(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$\Delta G^\circ = -RT \ln K$$
$$-690.9R = -R \times 300 \ln K$$
$$\frac{690.9}{300} = \ln K$$
$$2.303 = 2.303 \log K$$
$$K = 10$$
$$K_p = \frac{p^2(SO_3)}{p^2(SO_2) \text{ or } (p(O_2)} \cdot \frac{atm^2}{atm^2.atm}$$
$$= atm^{-1}$$

B102. (*d*) :
$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$
$$5.74 = 4.74 + \log \frac{\text{Conc.} \times \text{Volume (Salt)}}{\text{Conc.} \times \text{Volume (Acid)}}$$
$$5.74 - 4.74 = \log \frac{\text{Volume (Salt)}}{\text{Volume (Acid)}}$$
[Conc. are same]
$$1 = \log \frac{\text{Volume (Salt)}}{\text{Volume (Acid)}}$$

$\therefore$ Volume (salt) : Volume of (acid) = 10 : 1
or Volume (acid) : Volume (salt) = 1 : 10

B103. (*d*) : $2A \rightleftharpoons B + C$

Given
$$T = 300K, \Delta G^\circ = 2494.2 \text{ J}$$
$$R = -8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$
$$\Delta G^\circ = -2.303 \text{ RT} \log K_C$$
$$2494.2 = -2.303 \times 8.314 \times 300 \log K_C$$
$$\log K_C = -\frac{2494.2}{2.303 \times 8.314 \times 300} = -0.4342$$
$$K_C = \text{antilog } (-0.4342) = 0.3679$$
$$Q_C = \frac{[B][C]}{[A]^2} = \frac{2 \times \frac{1}{2}}{\left(\frac{1}{2}\right)^2} = 4$$

Since $Q_C > K_C$, the reaction will proceed in the backward direction.

B104. (*d*) : pH = – log [H⁺]
pH of 0.1 M strong monobasic acid,
pH = – log (10^{-1}) = 1
pH of resulting solution = 1 × 3 = 3
$$\therefore [H^+] = 10^{-3} = \frac{0.1}{100}$$
$\therefore$ Original solution is diluted 100 times.

B105. (*c*) : $MSO_4 . 2H_2O(s) \rightleftharpoons MSO_4(s) + 2H_2O(g)$

$$p_{(total)} = p(H_2O) = \frac{\pi}{4} \text{ atm}$$
$$K_p = [p(H_2O)]^2 = \left(\frac{\pi}{4}\right)^2 = \frac{\pi^2}{16} \text{ atm}^2$$

B106. (*c*) : $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$

$K_c = [Fe^{3+}][OH^-]^3$
Let the conc. of Fe^{3+} be x and that of $[OH^-]$ be y.
$K_c = (x)(y)^3$

On changing conc. of $[OH^-]$ by $\frac{1}{4}$ times,
$$[OH^-] = y' = \frac{1}{4} y$$
and let conc of Fe^{3+} be x'.
$$K'_c = x' \left(\frac{y}{4}\right)^3 = \frac{1}{64} x' y^3$$
Since equilibrium constant does not change with change in concentration, $K_c = K'_c$
$$x y^3 = \frac{1}{64} x' y^3$$
or $$x' = 64\, x$$
Thus, concentration of $[Fe^{3+}]$ increase by 64 times.

B107. (*d*) : (*i*) $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$ K_1

(*ii*) $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ K_2

Equation (*ii*) can be obtained by multiplying equation (*i*) by 2 and reversing it. Therefore,
$$K_2 = \frac{1}{K_1^2}$$

B108. (*c*) :

	A	+ B	⇌ C	+ D	; K = 100
Initial conc.	1	1	1	1	
At equi.	1–*x*	1–*x*	1+*x*	1+*x*	

$$K = \frac{[C][D]}{[A][B]} = \frac{(1+x)(1+x)}{(1-x)(1-x)}$$
$$\frac{(1+x)^2}{(1-x)^2} = 100$$
$$\frac{1+x}{1-x} = \sqrt{100} = 10$$
$$1 + x = 10 - 10x$$
$$x + 10x = 10 - 1 = 9$$
$$11x = 9$$
$$x = \frac{9}{11}$$
$$[D] = 1 + \frac{9}{11} = \frac{20}{11} = 1.818$$

B109. (*d*) : (*i*) $2H_2O \rightleftharpoons 2H_2 + O_2$ $K_1 = 6.4 \times 10^{-8}$
By reversing the eqn. and dividing by 2

(*ii*) $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$ $K_1' = \sqrt{\frac{1}{6.4 \times 10^{-8}}}$

(*iii*) $2CO_2 \rightleftharpoons 2CO + O_2$ $K_2 = 1.6 \times 10^{-6}$
By dividing by 2

(*iv*) $CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$ $K_2' = \sqrt{1.6 \times 10^{-6}}$
By adding eq. (*ii*) and (*iv*)
$H_2 + CO_2 \rightleftharpoons H_2O + CO$ $K = K_1' \times K_2'$
$$K = \sqrt{\frac{1.6 \times 10^{-6}}{6.4 \times 10^{-8}}} = \sqrt{25} = \mathbf{5}$$

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B111. (*c*) : Equilibrium constant is independent of the presence of catalyst.

B112. (*b*) : $\frac{3}{2}A \longrightarrow B;\ \Delta G^\circ = 163\ kJ\ mol^{-1}$

$$Q_c = \frac{[B]}{[A]^{3/2}} = \frac{1}{(10000)^{3/2}} = 10^{-6}$$

$$\Delta G^\circ = -RT\ \ln K_c$$

$$163\times10^3 = -8.314\times298\ \ln K_c$$

$$\text{or } 2.303\log K_c = -\frac{163\times10^3}{8.314\times298}$$

$$\log K_c = -\frac{163\times10^3}{8.314\times298\times2.303} = -28.57$$

$$\text{or } K_c = 2.69\times10^{-29}$$

Since $Q_c > K_c$, the reaction will move in the reverse direction.

B113. (*d*) : Hydrolysis of NaCN gives basic solution.

$$NaCN + H_2O \rightleftharpoons \underset{\text{Strong base}}{NaOH} + \underset{\text{Weak acid}}{HCN}$$

Hence, pH will be greater than 7.

B114. (*a*) : Let solubility of $PbCl_2$ is s mol L^{-1}.

$$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$$

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

$$(s)(2s)^2 = 1.8\times10^{-4}$$

$$4s^3 = 1.8\times10^{-4}$$

$$s^3 = \frac{1.8\times10^{-4}}{4} = 0.45\times10^{-4}$$

$$s = (0.45\times10^{-4})^{1/3}.$$

B115. (*b*) : For a salt of a weak acid and a weak base,

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

$$= 7 + \frac{1}{2}(3.2) - \frac{1}{2}(3.4)$$

$$= 7 + 1.6 - 1.7 = \mathbf{6.9}$$

B116. (*a*) : $A_2 \rightleftharpoons 2A$

Conc. at equilibrium

$$[A_2] = \frac{0.5}{5}$$

$$[A] = \frac{2\times10^{-6}}{5}$$

$$K_c = \frac{[A]^2}{[A_2]}$$

$$= \frac{\left[\frac{2\times10^{-6}}{5}\right]^2}{\frac{0.5}{5}} = 0.16\times10^{-11}$$

B117. (*b*) :

	$2HI(g)$	$\rightleftharpoons H_2(g)$	$+ I_2(g)$
Initial conc.	0.2	0	0
At equiv.	$(0.2-2x)$	x	x

$0.2 - 2x = 0.04$ atm

or $2x = 0.2 - 0.04 = 0.16$

or $x = 0.08$ atm

$$K_p = \frac{(0.08\times0.08)}{(0.04)^2} = 4$$

B118. (*b*) :

	N_2O_4	$\rightleftharpoons 2NO_2$
Initial conc.	1	0
At equiv.	$1-\alpha$	2α

Total moles at equilibrium $= 1 - \alpha + 2\alpha = 1 + \alpha$

$$p(N_2O_4) = \left(\frac{1-\alpha}{1+\alpha}\right)P;\ p(NO_2) = \left(\frac{2\alpha}{1+\alpha}\right)P$$

$$K_p = \frac{p(NO_2)^2}{p(N_2O_4)}$$

$$= \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2 P^2}{\left(\frac{1-\alpha}{1+\alpha}\right)P} = \frac{4\alpha^2}{1-\alpha^2}P$$

B120. (*d*) : $\Delta n_g = 1 + 1 - 0 = 2$

B122. (*b*) : $H_2S \rightleftharpoons H^+ + HS^-\ ;\ K_1 = 1.0\times10^{-7}$

$HS^- \rightleftharpoons H^+ + S^{2-}\ ;\ K_2 = 1.2\times10^{-13}$

For H_2S

$H_2S \rightleftharpoons 2H^+ + S^{2-}$

$K = K_1\times K_2 = 1.0\times10^{-7}\times1.2\times10^{-13} = 1.2\times10^{-20}$

Now $K = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$

$[H_2S] = 0.10$ M,

$HCl \longrightarrow H^+ + Cl^-\ ;\ [H^+] = 0.20$ M

$$1.2\times10^{-20} = \frac{[S^{2-}][0.20]^2}{0.10}$$

$$[S^{2-}] = \frac{1.2\times10^{-20}\times0.10}{(0.20)^2}$$

$$= 3.0\times10^{-20}$$

B123. (*c*) : Conc. of SO_4^{2-} ions in final solution,

$$M_1V_1 = M_2V_2$$

$$1\times50 = M_2\times500$$

$$\text{or } M_2 = \frac{1\times50}{500} = 0.1\ M$$

For just precipitation of $BaSO_4$,

Ionic product $= K_{sp}$

$$[Ba^{2+}][SO_4^{2-}] = 1\times10^{-10}$$

$$[Ba^{2+}][0.1] = 1\times10^{-10}$$

$$[Ba^{2+}] = \frac{1\times10^{-10}}{0.1} = 10^{-9}$$

For calculation of $[Ba^{2+}]$ in original solution (450 mL),

$$M_3V_3 = M_4V_4$$

$$10^{-9}\times500 = M_4\times450$$

$$M_4 = \frac{10^{-9}\times500}{450} = 1.1\times10^{-9}M$$

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B124. (*b*) : CH_3COOK is a salt of weak acid (CH_3COOH) and strong base (KOH) and therefore, its solution will be most basic.

$CH_3COOK \rightleftharpoons CH_3COO^- + K^+$

Acetate ion undergoes hydrolysis

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

(Basic)

B125. (*c*) : Methyl orange has pinkish red colour in acidic medium and yellow colour in basic medium. Since initial solution is basic so initial colour is yellow. For weak base and strong acid,

$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$

(weak) (strong)

At the end point, pH will be less than 7 and the solution will be acidic. The colour will be pinkish red.

B126. (*a*) : $\Delta G = \Delta H - T\Delta S$

$-RT \ln k = \Delta H - T\Delta S$

$$\ln k = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

The plot of $\ln k$ vs $1/T$ is a straight line.

$$\text{Slope} = -\frac{\Delta H}{R}$$

Since ΔH is negative (exothermic reaction), slope is +ve and therefore, lines should be A and B.

B127. (*c*) :

	A	+ 2B	$\rightleftharpoons$	2C	+ D
Intial	a_0	$1.5a_0$		0	0
Equiv.	$(a_0 - x)$	$(1.5a_0 - 2x)$		$2x$	x

At equilibrium, [A] = [B]

$a_0 - x = 1.5a_0 - 2x$

or $-x + 2x = 1.5a_0 - a_0$

$x = 0.5a_0$

So, at equilibrium

$[A] = a_0 - 0.5a_0 = 0.5a_0$

$[B] = 1.5a_0 - 0.5a_0 \times 2 = 0.5a_0$

$[C] = 2 \times 0.5a_0 = a_0$

$[D] = 0.5a_0$

$$K_c = \frac{[C]^2[D]}{[A][B]^2} = \frac{(a_0)^2 \times (0.5a_0)}{(0.5a_0) \times (0.5a_0)^2} = 4$$

B128. (*b*) : $Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$

Let solubility of Ag_2CO_3 in 0.1 M $AgNO_3$ be x mol L^{-1}

$[Ag^+] = 2x$, $[CO_3^{2-}] = x$

$AgNO_3$ dissociates as

$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$

In 0.1 M $AgNO_3$ solution,

$[Ag^+] = 0.1$ M, $[NO_3^-] = 0.1$ M

Total $[Ag^+] = 2x + 0.1 \simeq 0.1$ ($\because x$ is very small)

$K_{sp} = [Ag^+]^2[CO_3^{2-}]$

$8 \times 10^{-12} = (0.1)^2(x)$

$$x = \frac{8 \times 10^{-12}}{(0.1)^2} = 8 \times 10^{-10}$$

B129. (*c*) : HgS which has lowest K_{sp} value

B130. (*b*) : $NaX + H_2O \longrightarrow NaOH + HX$

HX is weak acid so NaX is a salt of weak acid and strong base

$$K_h = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{10^{-5}} = 10^{-9}$$

Now, $K_h = Ch^2$

$10^{-9} = 1.0 \times h^2$

$$h^2 = \frac{1.0 \times 10^{-9}}{0.1} = 10^{-8}$$

$h = 10^{-4}$

Percentage of hydrolysis

$= 10^{-4} \times 100 = 10^{-2}\%$ or 0.01 %

B131. (*b*):

	CH_3NH_2	+ HCl	$\longrightarrow$	$CH_3NH_3^+$	+ Cl^-
	0.1	0.08		0	
	0.02	0		0.08	

Basic buffer

$$pOH = pK_b + \log \frac{0.08}{0.02} \quad pK_b = -\log(5 \times 10^{-4})$$

$= 3.30$

$\therefore$ $pOH = pK_b + 0.602$

$= 3.30 + 0.602$

$= 3.902$

$pH = -\log(3.902)$

$= 10.09$

$[H^+] = -\log(10.09)$

$= 7.99 \times 10^{-11}$

or $= 8 \times 10^{-11}$M

B132. (*a*) : $K = K_f \times K'_f = 6.8 \times 10^3 \times 1.6 \times 10^3 = 1.08 \times 10^7$

B133. (*c*) :

	B^+	+ H_2O	$\rightleftharpoons$	BOH	+ H^+
	$c(1-h)$			ch	ch

For titration

$N_1V_1 = N_2V_2$

$$\frac{2}{15} \times V_1 = 2.5 \times \frac{2}{5}$$

$\therefore$ V_1 = Volume of HCl used, V = 7.5 mL

In resulting solution,

Conc. of salt = $[BCl] = \frac{2/5 \times 2.5}{10} = 0.1$

$$\frac{K_w}{K_b} = \frac{ch^2}{1-h} \text{ or } h = \sqrt{\frac{K_w}{K_b \times c}}$$

$$\sqrt{\frac{10^{-14}}{10^{-12} \times 0.1}} \Rightarrow h = \sqrt{\frac{1}{10}}$$

$[H^+] = ch = 0.1 \times \sqrt{\frac{1}{10}} = 3.2 \times 10^{-2}$M

B134. (*d*) : Solubility of MX, $s_1 = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}$

Solubility of MX_2,

$$s_2 = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{3.2 \times 10^{-14}}{4}\right)^{1/3} = 2 \times 10^{-5}$$

Solubility of MX_3, $s_3 = \left(\frac{2.7 \times 10^{-15}}{27}\right)^{1/4} = 10^{-4}$

$s_1 > s_3 > s_2 \Rightarrow MX > M_3X > MX_2$

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B135. (*a*) : Initial conc. of HCl = 10^{-1} M

Final conc. of HCl after dilution = 10^{-2} M

$$M_1V_1 \equiv M_2V_2$$
$$10^{-1} \times 1 \equiv 10^{-2} \times V_2$$
$$V_2 = \frac{0.1}{0.01} = 10 \text{ L}$$

Volume of water to be added = 10 – 1 = 9L.

B136. (*b*) : $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

If s is the solubility of Ag_2CrO_4

$[CrO_4^{2-}] = s$, $[Ag^+] = 2s + 0.1 \approx 0.1$

$$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$$
$$(0.1)^2 (s) = 1.1 \times 10^{-12}$$
$$s = \frac{1.1 \times 10^{-12}}{(0.1)^2}$$
$$= 1.1 \times 10^{-10} \text{ mol L}^{-1}$$

$\therefore$ Solubility of $Ag_2CrO_4 = 1.1 \times 10^{-10}$ mol L^{-1}.

C. *mcq with more than one correct answer*

C1.(*a,b*) ΔH should be +ve and reaction should have occurred with increase in number of gaseous moles.

C5.(*a,c*) Salts of strong acid and weak bases are acidic because of hydrolysis.

C10.(*a,b,d*) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

The equilibrium constant is independent of initial conc. of $CaCO_3$ (*b*); ΔH depends upon temperature (*a*), ΔH is independent of catalyst (*d*). But K is dependent on pressure of CO_2 at a given temperature.

D. *mcq based on comprehension*

D1. (*d*) $A_2X_3 \rightleftharpoons 2A^+ + 3X^-$

If solubility is y mol dm^{-3}

$[A] = 2y$, $[X^-] = 3y$

$K_{sp} = [A^+]^2 [X^-]^3 = (2y)^2 \times (3y)^3 = 108y^5$

D2.(*a*) $\frac{10^{-4}}{2} \times \frac{10^{-4}}{2} = \frac{1}{4} \times 10^{-8}$.

This is more than 1.8×10^{-10}.

D3.(*c*) The salt having lowest K_{sp} will precipitate out first *i.e.*, HgS.

D4. (*b*) $A_2B_3 \rightleftharpoons 2A^+ + 3B^-$

$K_{sp} = [A^+]^2[B^-]^3$

If s is the solubility,

$K_{sp} = (2s)^2 (3s)^3 = 108s^5$

$\therefore$ $108s^5 = 1.1 \times 10^{-23}$

$$s^5 = \frac{1.1 \times 10^{-23}}{108} = 1.0 \times 10^{-25}$$

$\therefore$ $s = 1.0 \times 10^{-5}$

D5.(*b*) $K_{sp} = [Fe^{3+}][OH^-]^3$

$[Fe^{3+}] = [FeCl_3] = 0.001$M

$$[OH^-]^3 = \frac{1 \times 10^{-36}}{0.001} = 1 \times 10^{-33}$$

$\therefore$ $[OH^-] = 1 \times 10^{-11}$

D6. (*a*) $pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log C$

$pK_a = -\log(1.8 \times 10^{-5}) = 4.745$

$\therefore$ $pH = \frac{1}{2}(14) + \frac{1}{2}(4.745) + \frac{1}{2}(-1)$

$= 7 + 2.3725 - 0.5 = 8.87$

D7. (*a*) $pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b$

$= \frac{1}{2} \times 14 = 7$ ($\because pK_a = pK_b$)

D8. (*c*) $pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b$

$= \frac{1}{2}(14) + \frac{1}{2}(9.02) - \frac{1}{2}(4.76) = 9.13$

D9. (*c*) pH of ammonium acetate is independent of conc.

D10. (*d*) $pH = \frac{1}{2} pK_a + \frac{1}{2} pK_a + \frac{1}{2} \log C$

$8.2 = \frac{1}{2}(14) + \frac{1}{2}(3.4) + \frac{1}{2} \log C$

$\frac{1}{2} \log C = 8.2 - 7 - 1.7 = -0.5$

$\log C = -0.5 \times 2 = -1$

$\therefore$ $C = 0.1$.

D11. (*b*)

	$X_2(g) \rightleftharpoons$	$2X(g)$
Initial	1	0
At equi.	$1 - \frac{\beta_{eq}}{2}$	β_{eq}

$$K_p = \frac{(p_X)^2}{p_{X_2}}$$

Now $p_{x_2} = \frac{1 - \frac{\beta_{eq}}{2}}{1 - \frac{\beta_{eq}}{2} + \beta_{eq}} p_{total} = \frac{1 - \frac{\beta_{eq}}{2}}{1 + \frac{\beta_{eq}}{2}} p_{total}$

$p_x = \frac{\beta_{eq}}{1 - \frac{\beta_{eq}}{2} + \frac{\beta_{eq}}{2}} p_{total} = \frac{\beta_{eq}}{1 + \frac{\beta_{eq}}{2}} p_{total}$

$\therefore$ $K_p = \left(\frac{\beta_{eq}}{1 + \frac{\beta_{eq}}{2}} p_{total}\right)^2 \Bigg/ \left(\frac{1 - \frac{\beta_{eq}}{2}}{1 + \frac{\beta_{eq}}{2}} p_{total}\right)$

$$= p_{total} \times \frac{(\beta_{eq})^2}{\left(1 + \frac{\beta_{eq}}{2}\right)^2} \times \frac{\left(1 + \frac{\beta_{eq}}{2}\right)}{\left(1 - \frac{\beta_{eq}}{2}\right)}$$

$$= p_{total} \times \frac{(\beta_{eq})^2}{\left(1 + \frac{\beta_{eq}}{2}\right)^2 \left(1 - \frac{\beta_{eq}}{2}\right)}$$

$$= 2\left(\frac{\beta_{eq}^2}{1 - \frac{\beta_{eq}^2}{4}}\right) = \frac{2\beta_{eq}^2}{\frac{4 - \beta_{eq}^2}{4}} = \frac{8\beta_{eq}^2}{4 - \beta_{eq}^2}$$

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D12. (*c*) (a) is correct because if *p* decreases the reaction will move in the forward direction (Le Chatelier principle)

(*b*) At the start of reaction, $Q_p < K_p$

$\Delta G = \Delta G^\circ + RT\ ln\ Q$

ΔG = – ve, so dissociation of gaseous X_2 takes place spontaneously. The statement is true.

(*c*) If $\beta = 0.7$

$$K_p = \frac{8\times(0.7)^2}{4-(0.7)^2} = \frac{3.92}{3.51}$$

$K_p > 1$

Since it is given, $\Delta G^\circ > 0$, so that $K_p < 1$

($\because \Delta G^\circ = -RT\ ln\ K_p$)

This is incorrect.

(*d*) $K_p = K_c (RT)^{\Delta n_g}$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{K_p}{(R\times 298)^1}$$

Now, ΔG° = +ve

$\Delta G^\circ = -RT\ ln\ K_p$

$\therefore$ $K_p < 1$

Since K_p <1, K_c is also less than 1.

Matching Type Questions

1. (*d*) :

P. $NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$

$$\text{Moles of NaOH} = \frac{0.1}{1000}\times 10 = 1 \text{ mmole}$$

$$\text{Moles of } CH_3COOH = \frac{0.1}{1000}\times 20 = 2 \text{ mmole}$$

Now solution contains 1mmol of CH_3COOH and 1mmole of CH_3COONa in 30 mL solution or 0.5 mmol of CH_3COOH and 0.5 mmol of CH_3COONa in 60 mL.

[Acid] = [Salt]

It is a buffer solution and pH does not change.

P $\longrightarrow$ 1.

Q. $NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$

2 mmol 2 mmol

Solution contains 2 mmol of CH_3COONa in 40 mL

$$[H^+]_{initial} = \sqrt{\frac{K_w.K_a}{c}}$$

On dilution upto 80 mL, conc. becomes c/2

$$[H^+]_{dil} = \sqrt{\frac{K_w.K_a}{c/2}} = \sqrt{\frac{2K_w.K_a}{c}}$$

or $= \sqrt{2}.[H^+]_{initial}$

Q $\longrightarrow$ 5.

R. $HCl + NH_3 \longrightarrow NH_4Cl$

2 mmol 2 mmol

Solution contains 2mmol of NH_4Cl in 40 mL

$$[H^+]_{initial} = \sqrt{\frac{K_w.c}{K_b}}$$

On dilution to 80 mL, conc. becomes c/2

$$\therefore\ [H^+]_{dilution} = \sqrt{\frac{K_w.c/2}{K_b}} = \frac{[H^+]_{initial}}{\sqrt{2}}$$

R $\longrightarrow$ 4.

S. $Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

It is sparingly soluble salt. On dilution, $[OH^-]$ conc. in saturated solution of $Ni(OH)_2$ remains constant.

Therefore, $[H^+]$ does not change.

S $\longrightarrow$ 1.

Integer Type Questions

1. (3) :

	PCl_5	$\rightleftharpoons$ PCl_3	+ Cl_2
Initial moles	1	0	0
Moles at eq.	1 – 0.5 = 0.5	0.5	0.5

If P is the total pressure,

$$p(PCl_3) = \frac{0.5}{1.5}P = \frac{P}{3}\ ;\ p(Cl_2) = \frac{0.5}{1.5}P = \frac{P}{3}$$

$$p(PCl_5) = \frac{0.5}{1.5}P = \frac{P}{3}$$

$$K_p = \frac{p(PCl_3)\times p(Cl_2)}{p(PCl_5)} = \frac{\frac{P}{3}\times\frac{P}{3}}{P/3} = \frac{P}{3}$$

or $P = 3K_p$

2. (8) : $Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$

3. (9) : $pH = -\log(10^{-5}) = 5$

$\therefore$ $pOH = 14 - 5 = 9$

4. (5) : $[H^+] = \frac{0.01}{1000} = 10^{-5}M$

$pH = -\log[H^+] = -\log(10^{-5}) = 5$

5. (5) : pH = 5.127

$\log[H^+] = -5.127$

$[H^+] = 7.46\times 10^{-6}$

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

If *h* is degree of hydrolysis

$[H^+] = ch$

or $h = \frac{7.46\times 10^{-6}}{0.1} = 7.46\times 10^{-5}$

6. (6) : pH of 10^{-2} M NaOH = 12

pH of 10^{-2} M HCl = 2

$$\therefore\ \frac{\text{pH (NaOH)}}{\text{pH (HCl)}} = 6$$

7. (9) : $pK_a + pK_b = 14$

$pK_b = 14 - pK_a = 14 - 5 = 9$

8. (4) : Amount of H_2SO_4 in 10L = 0.049 g

Molar concentration of H_2SO_4

$$= \frac{0.049\times 1}{98\times 10} = 5\times 10^{-5}\ M$$

$[H^+] = 2\times [H_2SO_4] = 2\times 5\times 10^{-5} = 1\times 10^{-4}$ M

$pH = -\log(1\times 10^{-4}) = 4.$

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9. (9) : $[OH^-] = 10^{-3}$ M

$$[OH^-] \text{ of diluted solution } = \frac{10^{-3}}{100} = 10^{-5}$$

$$pOH = -\log(10^{-5}) = 5$$

$$\therefore \quad pH = 14 - 5 = 9.$$

10. (4.47) : Refer Advanced Level Problems; Problem 8 (Page 92)

NCERT Exemplar Problems : MCQs Type I

1. (*d*) : $\Delta n_g = 1 + 1 - 0 = 2$

2. (*d*) : $\Delta G^\circ = -RT \ln K$

$\Delta G^\circ > 0$ means ΔG° is +ve. This can be only possible if K is –ve *i.e.* $K < 1$.

3. (*c*) : All physical processes donot stop at equilibrium.

4. (*b*) : $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(1.2 \times 10^{-3}) \times (1.2 \times 10^{-3})}{(0.8 \times 10^{-3})}$

$= 1.8 \times 10^{-3}$ mol L^{-1}.

5. (*b*) : $Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$ (red)

When oxalic acid is added, it combines with Fe3+ ions. As a result, equilibrium shifts in the backward direction and intensity of red colour decreases.

6. (*a*) : Since the reaction shifts to backward direction on cooling, this means that the backward reaction is exothermic reaction. Therefore, the forward reaction is endothermic reaction and $\Delta H > 0$.

7. (*a*) : As the ionisation of water increases, the concentration of H^+ ions increases and therefore, pH will be less than 7.0.

8. (*d*) : $[H_3O^+] = \sqrt{K_a \cdot C}$ For the same concentration, $[H_3O^+] \propto \sqrt{K_a}$. But $pH = -\log [H_3O^+]$

Larger the value of K_a, larger will be $[H_3O^+]$ and lower will be pH.

9. (*a*) : $K_{a_3} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{[H^+][HS^-]}{[H_2S]} \times \frac{[H^+][S^{2-}]}{[HS^-]}$

$= K_{a_1} \times K_{a_2}$

10. (*c*) : BF_3 is Lewis acid because it accepts electrons.

11. (*c*) : Because it will form weak base and salt of weak base.

12. (*d*) : AgCl will be most soluble in aqueous ammonia because it forms a complex, $[Ag(NH_3)_2]^+Cl^-$.

13. (*a*) : $[H_3O^+] = \sqrt{K_a \cdot C}$

$$= \sqrt{1.74 \times 10^{-5} \times 0.01} = 4.17 \times 10^{-4}$$

$$pH = -\log(4.17 \times 10^{-4}) = 3.4$$

14. (*c*) : Both are weak of equal strength. Therefore, these will neutralise to form neutral solution of pH = 7.

15. (*a*) : $\Delta G^\circ = -2.303\ RT \log K$

At stage of half completion of reaction [A] = [B]. Therefore, K = 1 and $\Delta G^\circ = 0$.

16. (*a*) : According to Le-Chatelier principle, at constant temperature the equilibrium composition will change but K will remain same.

17. (*b*) : Greater the boiling point, less is the vapour pressure. Hence, correct order of vapour pressure is : water < acetone < ether.

18. (*a*) : $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)\ K_a = 5$

$$HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)\ K_a = \frac{1}{5}$$

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)\ K_a = \left(\frac{1}{5}\right)^2 = 0.04$$

19. (*d*) : Addition of small amount of argon does not affect any of these reactions.

NCERT Examplar Problems : MCQs Type II

20. (*a*, *c*, *d*) : (*a*) K increases with increase in temperature.

(*c*) Since Q is larger than K, therefore, reaction proceeds in the backward direction.

(*d*) Since Δn_g is +ve, ΔS will increase.

21. (*a*, *d*) : Solid $\rightleftharpoons$ Liquid

Equilibrium exists at normal melting point or normal freezing point.

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Unit Practice Test

for Board Examination

Time Allowed : 1 Hr. ***Maximum Marks : 25***

1. Write the expression K_p for the reaction :

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$ (1)

2. State the conjugate acid—base pairs in the following reaction.

$$CO_3^{2-} + H_2O \rightleftharpoons OH^- + HCO_3^-$$ (1)

3. Which of the following are Lewis acids?

$H_2O, BF_3, H^+, CN^-, CO_2$ (1)

4. The value of K_c for the reaction :

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-12}, what is the concentration of O_3? (1)

5. What is the value of K_p/K_c for the reaction :

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2$$ (1)

6. The solubility of $Sr(OH)_2$ at 298 K is 19.32 g L^{-1} of solution. Calculate the pH of the solution. (2)

7. How much sodium acetate should be added to 1L of 0.1 M CH_3COOH to make a buffer of pH = 4.0? $[K_a(CH_3COOH)] = 1.8 \times 10^{-5}$. (2)

8. At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass :

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

Calculate the K_c for this reaction at the given temperature. (2)

9. The solubility products of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of molalities of their saturated solutions. (3)

10. A 0.02 M solution of pyridinium hydrochloride has a pH of 3.44. Calculate the ionization constant of pyridine. (3)

11. The pH of 0.1 M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution. (3)

12. (*a*) State the Le-Chatelier principle and discuss its application in the manufacture of ammonia by Haber's process.

(*b*) Explain : the degree of hydrolysis of an aqueous solution of a salt of a weak acid and a weak base is independent of initial concentration of the salt.

(*c*) What is common ion effect? Give its one application. (2,2,1)

▶ To check your performance, see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part I of the book.

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Test Your

Learning Ability

According to Completely CBSE Pattern

MOCK TEST – 1

Time allowed : 3 hours ***Maximum Marks : 70***

General Instructions :

(*i*) *All questions are compulsory.*
(*ii*) *Question nos. 1 to 5 are very short answer questions and carry 1 mark each.*
(*iii*) *Question nos. 6 to 12 are short answer questions and carry 2 marks each.*
(*iv*) *Question 13 to 24 are also short answer questions and carry 3 marks each.*
(*v*) *Question nos. 25 to 27 are long answer questions and carry 5 marks each.*
(*vi*) *Use log tables if necessary. Use of calculators in not allowed.*

1. How many electrons in an atom may have the following quantum numbers?
$n = 4, l = 2, m_l = 0, m_s = -1/2$ (1)

2. The equilibrium constant for the reaction :
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); K_p = 2.5 \times 10^{20}$
What is the value of equilibrium constant for the reaction :
$3SO_2(g) + \frac{3}{2}O_2(g) \rightleftharpoons 3SO_3(g)$ (1)

3. For the process to occur adiabatically, the correct condition is that $\Delta T = 0$. Is the statement correct or wrong? (1)

4. Ice melts slowly at higher altitudes. Why? (1)

5. Which of the following state of bromine will have standard heat of formation to be equal to zero ?
Br_2 (s) , Br_2(l), Br_2(g) (1)

6. If the density of methanol (CH_3OH) is 0.806 kg L^{-1}, what is the volume needed for making 2.5 L of its 0.50 M solution? (2)

7. The wavelength of first spectral line in Balmer series is 6561Å. Calculate the wavelength of the second spectral line in Balmer series. (2)

8. The species H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and base. (2)

9. K_p for the following conversion reaction :
$\frac{3}{2}O_2(g) \longrightarrow O_3(g)$ at 298 K is 2.47×10^{-29}. What is $\Delta_r G^\circ$ for this reaction ? (2)

10. Ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature? (2)

11. How does the rate of evaporation relate to nature of the liquid ?

12. State Le-Chatelier's principle.

13. (*a*) What are ideal and non-ideal gases? List important differences between them. Write an equation for a non-ideal gas. (2)
(*b*) A spherical balloon of 10.5 cm radius is to be filled with hydrogen gas at N.T.P. from a cylinder containing the gas at 20 atm pressure and 27°C. If the cylinder can hold 2.82 litres of water, calculate the number of balloons that can be filled up. (3)

14. Explain the following :
(*a*) Evaporation leads to cooling
(*b*) Viscosity of a liquid decreases with rise in temperature.
(*c*) All gases cannot be liquefied at room temperature. (3)

15. The kinetic gas equation is $pV = \frac{1}{3}mN\overline{u^2}$. How will you explain the following gas laws with the help of this equation:
(*i*) Boyle's law
(*ii*) Dalton's law (3)

16. (*a*) Define ionization enthalpy. Explain is variaion along a period and down a group.
(*b*) How would you explain the fact that 'the first ionisation enthalpy of sodium is lower than that of magnesium but its second ionisation enthalpy is higher than that of magnesium'. (2)

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17. (*a*) Consider the following ions :

$Al^{3+}, Mg^{2+}, Na^{+}, F^{-}, O^{2-}$ and N^{3-}

(*i*) What is common in them?

(*ii*) Arrange them in the increasing order of ionic radii. (2)

(*b*) Which of the following has higher dipole moment in each of the following pair:

(*i*) OCS or CS_2

(*ii*) NF_3 or NH_3 (2)

18. With the help of molecular orbital energy level diagram explaing the following :

(*i*) O_2 molecule is paramagnetic.

(*ii*) Ne_2 molecule does not exist.

(*iii*) N_2^+ has less bond strength than N_2. (3)

19. A photon of wavelength 4×10^{-7} m strikes on a metal surface having the work function 2.13 eV. Calculate

(*i*) the kinetic energy of the photon (in eV)

(*ii*) kinetic energy of the emission

(*iii*) velocity of photoelectron (1 eV = 1.602×10^{-19} J) (3)

20. (*a*) Define bond enthalpy. How does it differ from bond dissociation enthalpy

(*b*) Calculate the enthalpy change for the reaction :

$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$

The average bond enthalpies of various bonds are :

	C—C	C—H	C=O	O=O	O—H
(kJ mol^{-1})	347	414	741	498	464

(3)

21. Define the following

(*i*) Entropy of fusion

(*ii*) Entropy of vaporization

(*iii*) Entropy of sublimation

How are these related? (3)

22. Calculate

(*i*) the hydrolysis constant

(*ii*) degree of hydrolysis

(*iii*) the pH of 0.1M sodium acetate solution.

The dissociation constant of CH_3COOH at room temperature is 1.8×10^{-5}. (3)

23. (*a*) Define Le-Chatelier principle. Explain the effect of pressure on equilibrium constant. (3)

(*b*) Define the following

(*i*) Entropy of fusion

(*ii*) Entropy of vaporization

(*iii*) Entropy of sublimation

How are these related? (3)

24. K_{sp} values of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of their molarities of the saturated solutions. (3)

25. What is meant by empirical formula and molecular formula? Give examples. How are they related to each other?

A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g of carbon dioxide, 0.690 g of water and no other products. A volume of 10.0L (measured at S.T.P.) of this welding gas is found to weigh 11.6g. Calculate (*i*) empirical formula (*ii*) molecular formula.

Or

What is meant by limiting reagent? Explain with an example.

Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation:

$$N_2(g) + 3\,H_2(g) \longrightarrow 2NH_3(g)$$

(*i*) Calculate the mass of ammonia produced if 2.00×10^3 g of dinitrogen reacts with 1.00×10^3 g of dihydrogen.

(*ii*) Will any of the two reactants remain unreacted?

(*iii*) If yes, which one and what would be its mass?

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26. What is Heisenberg's uncertainty principle? Explain. (5)

If the position of the electron is measured within an accuracy of ± 0.002 nm, calculate the uncertainty in the momentum of the electron. If suppose the momentum of the electron is $\frac{h}{4\pi m} \times 0.05$ nm, is there any problem in defining this value.

Or

(*a*) State the following :

(*i*) Hund's rule

(*ii*) Aufbau principle

(*iii*) Pauli exclusion principle

(*b*) Give the significance of the following quantum numbers.

(*i*) Magnetic quantum number

(*ii*) Angular quantum number.

27. (*a*) What is solubility product? How is it different from ionic product? How can it be used to calculate the solubility of a salt like AB_2?

(*b*) Explain :

(*i*) all Bronsted bases are also Lewis bases but all Bronsted acids are not Lewis acids.

(*ii*) pH of 10^{-7} M HCl is not exactly seven.

(*c*) How does an equilibrium constant predict the extent of the reaction. Explain. (5)

Or

(*a*) What is common ion effect ? Explain with examples.

(*b*) Account for dynamic nature of equilibrium.

(*c*) The ionization constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}. How many times silver benzoate is more soluble in buffer solution of pH 3.19 compared to its solubility in pure water.

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Hints & Solutions for *Unit Practice Tests & Mock Test*

UNIT PRACTICE TEST–1

1. 0.667
2. $\frac{12}{6.022\times10^{23}} = 1.9927 \times 10^{-23} g$
3. 29.3
5. $°C = \frac{5}{9}(°F–32) = \frac{5}{9}(98.6 – 32) = 37°C$

   $K = 273.15 + 37 = 310.15K$
6. 58.7
7. (*i*) 10.4 (*ii*) 0.0460 (*iii*) 5.00×10^3 (*iv*) 2810
8. Mass of drop of water = $0.448 \times 1 = 0.448$ g

   No. of molecules of water = $\frac{0.448\times6.022\times10^{23}}{18}$

   $= 1.5 \times 10^{22}$

   No. of hydrogen atoms = $1.5 \times 10^{22} \times 2$

   $= 3.0 \times 10^{22}$
9. (*i*) $C(s) + O_2(g) \longrightarrow CO_2(g)$

   Since only 16 g of dioxygen are available (0.5 mol), it will react with only 0.5 mol of C. Therefore, O_2 is the limiting reagent. Thus, 0.5 mol of C will be burnt to give 0.5 mol of CO_2 producing 22 g of CO_2.

   (*ii*) 4
10. 204.167 g (*refer Solved Example 84*)
11. (*i*) 17.5 M (*ii*) 71 mL (*refer Solved Example 117*)
12. Relation = Molecular formula = $(\text{Empirical formula})_n$

    $Na_2SO_4.10H_2O$ (*refer Solved Example 65*)

UNIT PRACTICE TEST–2

1. This means that the electrons in an atom can have only definite values of energy.
2. $E = h\nu$

   $E = (6.6 \times 10^{-34}\ Js) \times (3.0 \times 10^{15}\ s^{-1}) = 1.98 \times 10^{-18}$ J
3. Protons = 92, Neutrons = 235 – 92 = 143
4. An electron because it has smaller mass than the proton ($\lambda = \frac{h}{mv}$)
5. 4*d*
6. $n = 4, l = 3, m_l = –3, –2, –1, 0, +1, +2, +3$
7. *Refer Solved Example 52*
8. (*i*) Cr(Z = 24) :

   Six unpaired electrons

   (*ii*) Fe (Z = 26) :

   Four unpaired electrons
9. Orbital is a region in space around the nucleus where the probability of finding the electron is maximum. Both 1*s* and 2*s* orbitals are spherically symmetrical. 2*s* orbital is larger in size than 1*s* orbital. 2*s* orbital has two most probable regions whereas 1*s* orbital has only one most probable region. 2*s* orbital has one node whereas 1*s* orbital has no nodes.
10. Uncertainty in velocity,

    $\Delta v = \frac{600\times0.025}{100}$

    $= 0.15\ ms^{-1}$

    $\Delta x \times m\Delta v \geq \frac{h}{4\pi}$

    $\Delta x \geq \frac{h}{4\pi.m\Delta v}$

    $\geq \frac{6.6\times10^{-34}}{4\times\frac{22}{7}\times9.11\times10^{-31}\times0.15}$

    $\geq 3.84 \times 10^{-4}$ m
11. The lines obtained in the spectrum of hydrogen atom when the electron jumps to second energy level (n = 2) from higher energy levels (n = 3, 4, 5, 6.....) falling in visible region.

    $\bar{\nu} = 1.097 \times 10^7 m^{-1}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$

    For Balmer series, $n_1 = 2$, for longest wavelength; $\bar{v}$ should be minimum so that $n_2 = 3$

    $\bar{\nu} = 1.097 \times 10^7\left(\frac{1}{2^2}-\frac{1}{3^2}\right)m^{-1}$

    $= 1.097 \times 10^7 \times \frac{5}{36}\ m^{-1}$

    $= 1.523 \times 10^6\ m^{-1}$

    For shortest wavelength $\bar{\nu}$ should be maximum,

    $n_2 = \infty$

    $\bar{\nu} = 1.097 \times 10^7\left(\frac{1}{2^2}-\frac{1}{\infty}\right)$

    $= 1.097 \times 10^7 \times \frac{1}{4}$

    $= 2.74 \times 10^6\ m^{-1}$
12. (*a*) *Refer Text Page 6-7*

    (*b*) Angular momentum = $\frac{h}{2\pi}\sqrt{l(l+1)}$

    For 2*s*, $l = 0$

    $\therefore$ Angular momentum = 0

    (*c*) $n = 4, m_s = +1/2 = 16$ electrons

    (*d*) It measures the electron probability density at a point in an atom.

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Solution File

UNIT PRACTICE TEST–3

1. O
2. Cl
3. I^+
4. *d* and *p*
5. K > Mg > Al > B
6. *Refer Conceptual Questions Q.9 (page 39)*
7. *Refer NCERT File Q.21 (page 44)*
8. (*i*) F (*ii*) Cl (*iii*) P (*iv*) B
9. (*i*) ns^2np^{1-6} (*ii*) $5f^{1-14}\,6d^{0-1}\,7s^2$
10. (*i*) F, Na (*ii*) F, Na (*iii*) O, S
11. (*a*) C (*b*) D (*c*) A
12. (*a*) Oxygen has four electrons in 2*p* orbitals and two of the four 2*p* electrons must occupy the same 2-*p* orbital resulting in increased electron-electron repulsion. On the other hand, N has stable half-filled configuration, while F has greater nuclear charge. Therefore, O has ionization enthalpy less than N as well as F.

    (*b*) Elements in same group have similar properties because they have similar outer electronic configurations. For detal, *please refer text* (page 18-19).

    (c) A cation is formed by the loss of one or more electrons from the gaseous atom. With the loss of electrons from an atom, the magnitude of the nuclear charge remains same while the number of electrons decreases. As a result, the same nuclear charge now acts on lower number of electrons and therefore, the effective nuclear charge per electron increases. As a result, electrons are more strongly attracted and are pulled towards the nucleus and therefore, the size decreases. The anion is formed by the gain of one or more electrons and therefore, the number of electrons increases while the magnitude of nuclear charge remains same. As a result, the electrons are less tightly held by the nucleus and therefore, the size increases.

13. (*a*) According to Mendeleev's periodic law, the physical and chemical properties of the elements are periodic function of their atomic weight. On the other hand, according to modern periodic law, the properties are periodic function of their atomic number.

    (*b*) In general, on moving across a period from left to right, the basic character of oxides decreases while the acidic character increases. For example, on moving across the third period, it is observed that Na_2O is strongly basic, MgO is less basic, Al_2O_3 is amphoteric, SiO_2 is weakly acidic, P_2O_5 is acidic, SO_3 is strongly acidic while Cl_2O_7 is very strongly acidic as shown below :

    Na_2O : Strongly basic
    MgO : Basic
    Al_2O_3 : Amphoteric
    SiO_2 : Weakly acidic
    P_2O_5 : Acidic
    SO_3 : Strongly acidic
    Cl_2O_7 : Very strongly acidic

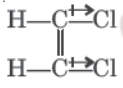
    The change from basic to acidic character takes place because of increasing electronegativity of the element as we move along a period.

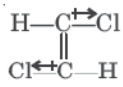
    (*c*) As we move in a period from left to right, the metallic character decreases while non-metallic character increases. For example, Li is the strongest metal and F is the strongest non-metal.

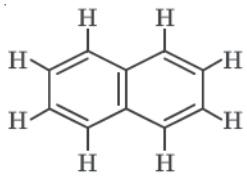
    $\underbrace{\text{Li}\quad\text{Be}}_{\text{Metals}}\qquad\underbrace{\text{B}}_{\text{Metalloid}}\qquad\underbrace{\text{C, N, O, F, Ne}}_{\text{Non metals}}$

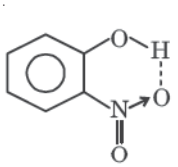
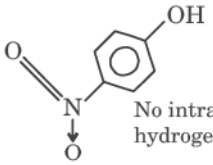
    This decrease in metallic character across a period is due to decreasing tendency to lose electrons (increasing ionisation enthalpy) and increasing tendency to gain electrons (increasing negative electron gain enthalpy)

UNIT PRACTICE TEST–4

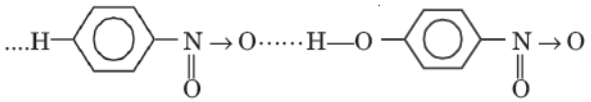
1. Both have same bond order 2.5
2. $N_2 < SO_2 < ClF_3 < K_2O < LiF$
3. Hybridisation of B changes from sp^2 to sp^3 while sp^3 hybridisation of N remains same.
4. *cis*  Resultant $\mu \neq 0$

    trans  Resultant $\mu = 0$

    cis – $C_2H_2Cl_2$ will have dipole moment.
5.  $\sigma = 19, \pi = 5$
6. *Refer NCERT File Q.23 (page 74)*
7. Both have hydrogen bonding. *o*-nitrophenol has **intramolecular** hydrogen bonds. But due to larger distance between $—NO_2$ and —OH groups in *p*-nitrophenol, there is no such bonding.

    
    
    No intramolecular hydrogen bonding

    However, there is intermolecular hydrogen bonding in *p*-nitrophenol and therefore, it exists as associated molecule. In *o*-nitrophenol, no intermolecular hydrogen bonding is possible.

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Solution File

Due to associated nature of *p*-nitrophenol, it is less volatile and has high boiling point.

8. O_2 : $KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\overset{*}{\pi} 2p_x)^1 (^*\pi 2p_y)^1$

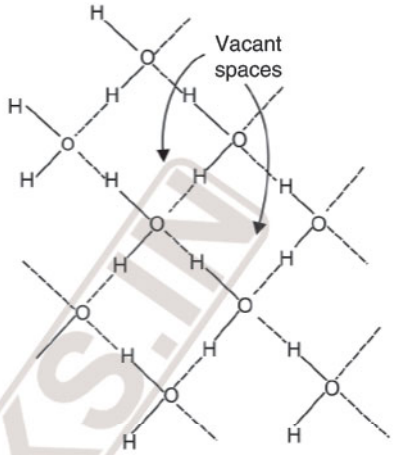
$$\text{B.O.} = \frac{8-4}{2} = 2$$

Superoxide ion, O_2^- : $KK(\sigma 2s)^2 (\overset{*}{\sigma} 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\overset{*}{\pi} 2p_x)^2 (\overset{*}{\pi} 2p_y)^1$

$$\text{B.O.} = \frac{8-5}{2} = 1.5$$

Bond order of $O_2 > O_2^-$

9. (*i*) SF_4, see saw geometry *refer* Fig. 15.
   (*ii*) ClF_3, T shape geometry *refer* Fig. 16.
   (*iii*) H_2O, V shape geometry *refer* Fig. 14.
10. (*i*) Ionic compounds have high melting and boiling points. This is because the ions are held together by strong electrostatic forces of attractions and hence large amount of energy is required to break the crystal lattice.
   (*ii*) X-ray studies have shown that in ice each oxygen atom is tetrahedrally surrounded by four hydrogen atoms in such a way that two hydrogen atoms are linked to oxygen atom by covalent bonds. These hydrogen atoms lie closer to the oxygen atom at a distance of 1.00 Å. The other two hydrogen atoms are linked to the central oxygen atom by hydrogen bonds. They lie away from oxygen atom at a distance of 1.76 Å . The oxygen atoms of water molecules are located at the corners of tetrahedron.



As a result of tetrahedral arrangement of H_2O molecules in the solid state, the ice structure extends in three dimensions.

Since hydrogen bonds between oxygen and H atoms are longer than the covalent bonds between them, the molecules of H_2O are not packed closely, but there are vacant spaces present in the crystal structure. This gives rise to an open cage like structure for ice having a larger volume for the given mass of water. Consequently, the density of ice is less than water and it floats over water.

(*iii*) BeH_2 molecule is linear molecule, therefore, resultant dipole moment of two Be—H bonds gets cancelled giving zero dipole moment to the molecule.

$$H \rightarrow Be \leftarrow H \qquad \mu = 0$$

11. *Refer text page 28-29*
12. (*a*) *Refer Text page 19*

$$O{=}C{=}O \longleftrightarrow {}^-O{-}C{\equiv}O^+ \longleftrightarrow O^+{\equiv}C{-}O^-$$

(*b*) *Refer Text Fig. 35 and 38.*
(*c*) (*i*) $P - sp^3d$ (*ii*) $S - sp^3d^2$.

UNIT PRACTICE TEST–5

1. The total pressure exerted by a mixture of two or more non-reacting gases in a definite volume is equal to the sum of the individual partial pressures which each gas would exert if it occupies the same volume alone at a constant temperature.
2. Gases have the property of diffusion which is independent of the force of gravitation. Due to diffusion, the gases mix into each other and remain almost uniformly distributed in the atmosphere.
3. Van der Waals constant '*a*' is a measure of the magnitude of intermolecular forces and constant '*b*' is a measure of the effective size of the molecules.
4. Both decrease with increase in temperature.
5. Because their critical temperature is lower than the room temperature. Gases cannot be liquefied above their critical temperature by applying even very high pressure.
6. *Refer Solved Example 28. (Ans. 3.0 g dm^{-3})*
7. *Refer Solved Example 24. (Ans. 40)*
8. The two faulty assumptions in the kinetic theory of gases which are responsible for deviation from ideal behaviour of gases are :
   (*i*) The molecules were considered as point masses and the volume occupied by the gas molecules is negligible in comparison to the total volume of the gas.
   (*ii*) It was assumed that there are no intermolecular forces between the molecules and they move independently.
9. *Refer Solved Example 25 (Ans. 202.8 mL)*
10. (*a*) Molar mass of an ideal gas can be calculated from the ideal gas equation as :

$$pV = nRT \quad \text{or} \quad p = \frac{nRT}{V}$$

Now, number of moles (n)

$$= \frac{\text{Mass of substance } (m)}{\text{Molar mass (M)}}$$

$$\therefore \quad = \frac{mRT}{M}$$

But mass per unit volume is density, *i.e.* $\frac{m}{V} = d$

where d is the density of gas.

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$$p = \frac{dRT}{M}$$

or $$M = \frac{dRT}{p}$$

(*b*) $$E_k = \frac{3}{2} nRT$$

$$n = \frac{4}{32} = \frac{1}{8} \text{ mol}$$

$$T = 273 - 13 = 260 \text{ K}$$

$$E_k = \frac{3}{2} \times \frac{1}{8} \times 8.314 \times 260$$

$$= \mathbf{405.3\ J}$$

11. *Refer Text page 46-47.*

12. The quantity $\frac{pV}{nRT}$ is called compressibility factor. For ideal gases it is equal to 1 but for other gases it may be greater than 1 or less than 1. If the gas is more compressible than expected from ideal behaviour, Z is less than 1. But if the gas is less compressible than expected from ideal behaviour, Z is greater than 1.

$$Z = \frac{pV}{nRT}$$

$n = 1$ mol, $p = 4 \times 10^6$ Pa, V = 320 mL = 0.320×10^{-3} m^3

T = 27 + 273 = 300 K, R = 8.314 Nm K^{-1} mol^{-1}

$$Z = \frac{4 \times 10^6 \times 0.320 \times 10^{-3}}{1.0 \times 8.314 \times 300}$$

$$= 0.513$$

UNIT PRACTICE TEST–5A

1. 12
2. Diamond is a network solid with strong interatomic forces whereas sulphur is a molecular solid consisting of puckered eight membered rings (S_8) held together by weak van der Waals forces.
3. Because the ions of alkali metals cannot get into the interstitial sites due to their larger size.
4. Group 15 (e.g., P or As)
5. Quartz is a crystalline solid in which SiO_4 tetrahedral units are arranged in an orderly arrangement. Quartz glass is an amorphous solid in which SiO_4 tetrahedral units are not arranged in any regular order.
6. Let M^{2+} ions in the crystal be x so that M^{3+} ions in the crystal will be $0.96 - x$. Total charge on the compound must be zero, so that

$$+2 \times x + 3(0.96 - x) - 2 = 0$$

$$2x - 2.88 - 3x - 2 = 0$$

$$x = 0.88$$

$$\therefore \quad \% \text{ of } M^{2+} = \frac{0.88}{0.96} \times 100 = 91.67$$

$$\% \text{ of } M^{3+} = 100 - 91.67 = 8.33.$$

7. In Schottky defect, density is markedly lowered while Frenkel defect does not affect the density of the crystal.
9. Edge length of the unit cell = 288 pm = 288×10^{-10} cm

Volume of the unit cell = $(288 \times 10^{-10})^3$ cm^3 = 2.39×10^{-23} cm^3

Mass of element = 208 g

Density of element = 7.2 g cm^{-3}

$$\text{Volume of 208 g of the element} = \frac{\text{Mass}}{\text{Density}}$$

$$\text{Mass of an atom} = \frac{208 \text{ g}}{7.2 \text{ g cm}^{-3}} = 28.89 \text{ cm}^3$$

Number of unit cells in this volume =

$$= \frac{\text{Volume of element}}{\text{Volume of unit cell}}$$

$$= \frac{28.89 \text{ cm}^3}{2.39 \times 10^{-23} \text{cm}^{-3} / \text{ unit cell}}$$

$$= 12.08 \times 10^{23} \text{ unit cells}$$

Since the structure is *bcc*, number of atoms present in a unit cell = 2

The number of atoms in 208 g of the element

$$= 2 \times 12.08 \times 10^{23} = 24.16 \times 10^{23} \text{ atoms}$$

or $$= \mathbf{2.416 \times 10^{24}\ atoms}$$

10. (*i*) This is because of some crystallisation in that region.

(*ii*) On heating, zinc oxide loses oxygen as :

$$ZnO \xrightarrow{\text{Heat}} Zn^{2+} + \frac{1}{2} O_2 + 2e^-$$

The zinc ions thus formed are entrapped into the interstitial sites while the electrons are entrapped in the neighbouring interstitial sites. The entrapped electrons enhance the electrical conductivity of ZnO.

(*iii*) $CdCl_2$ on adding to AgCl introduces impurity defect. The addition of one Cd^{2+} ion will replace two Ag^+ ions to maintain electrical neutrality. One of the position of Ag^+ ion will be occupied by Cd^{2+} ion and other will be left as a hole. Thus, a hole is created similar to Schottky defect.

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Solution File

UNIT PRACTICE TEST–6

1. $q + w$ is equal to ΔU, which is a state function.
2. Enthalpy of formation of NH_3 is :

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$$

$$\therefore \quad \Delta_f H^\circ = -\frac{92.2}{2} = -46.1 \text{ kJ mol}^{-1}$$

3. Enthalpy is a state function and is independent of the path followed.
4. At equilibrium, $\Delta S = 0$
5. $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$
6. $\Delta G = \Delta H - T\Delta S = 0$

or $$T = \frac{\Delta H}{\Delta S}$$

$$= \frac{450 \text{ kJ mol}^{-1}}{0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}} = 2250 \text{ K}$$

For the reaction to be spontaneous i.e., for ΔG to be –ve, T should be greater than 2250 K.

8. *Refer Solved Example 31.* (Ans. –84.4 kJ)
9. (*i*) decrease (*ii*) increase (*iii*) decrease
10. *Refer Solved Example 72* (Ans. –790.0 kJ mol^{-1})
11. *Refer Solved Example 44*

UNIT PRACTICE TEST–7

1. $K_p = p_{CO_2}$
2. CO_3^{2-}, HCO_3^- and H_2O, OH^-
3. BF_3, H^+, CO_2
4. $$K_c = \frac{[O_3]^2}{[O_2]^2}$$

$$2.0 \times 10^{-50} = \frac{[O_3]^2}{\left(1.6 \times 10^{-2}\right)^3}$$

$$\therefore \quad [O_3] = 2.86 \times 10^{-28} \text{ M}$$

5. $\frac{K_p}{K_c} = RT$

6. $Sr(OH)_2 \rightleftharpoons Sr^{2+} + 2OH^-$

$$\text{Solubility} = \frac{19.23}{121.6} = 0.1581 \text{ M}$$

$$[OH^-] = 2 \times 0.1581 = 0.3162 \text{ M}$$

$$[H_3O^+] = \frac{1 \times 10^{-14}}{0.3162} = 3.168 \times 10^{-14}$$

$$pH = -\log [H_3O^+] = -\log (3.168 \times 10^{-14})$$

$$= 13.5$$

7. *Refer Solved Example 88.* (Ans. 1.8×10^{-2} mol/litre)
8. *Refer Solved Example 22.* (Ans. 0.153)
9. *Refer Solved Example 101.* (Ans. 91.9 times)
10. *Refer Solved Example 84* (Ans. 1.52×10^{-9})

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Mock Test – 1

1. One

2. $(2.5 \times 10^{10})^{3/2} = 3.95 \times 10^{15}$

3. Wrong

4. The melting of ice

$$\text{Ice}(s) \rightleftharpoons \text{Water}(l)$$

is formed at high pressure because there is decrease in volume in the forward direction. Since at high altitudes, the atmospheric pressure is low, therefore, ice melts slowly.

5. $Br_2(l)$

6.
$$\text{Molarity} = \frac{\text{Moles of } CH_3OH}{\text{Volume in L}}$$

$$0.50 = \frac{\text{Moles of } CH_3OH}{2.5 \text{ L}}$$

$$\text{Moles of } CH_3OH = 0.50 \times 2.5 = 1.25 \text{ moles}$$

$$\text{Mass of } CH_3OH = 1.25 \times 32 = 40 \text{ g}$$

Now 0.806×10^3 g of CH_3OH are present in 1000 mL

40 g of CH_3OH will be present in

$$= \frac{1000}{0.806 \times 10^3} \times 40$$

$$= \mathbf{49.62 \text{ mL}}.$$

7. *Refer Chapter-2, Solved Example 39.*

8. *Refer Chapter-7, Solved Example 40.*

9. 163.2 kJ mol^{-1}.

10. $K_w = [H_3O^+][OH^-] = 2.7 \times 10^{-14}$

For neutral water $[H_3O^+] = [OH^-]$

$$[H_3O^+]^2 = 2.7 \times 10^{-14}$$

$$[H_3O^+] = 1.643 \times 10^{-7}$$

$$\text{pH} = -\log(1.643 \times 10^{-7})$$

$$= 6.75$$

11. Rate of evaporation varies with the nature of the liquid.

This depends upon the magnitude of the intermolecular forces such as :

Nature of liquid	Attractive forces	Evaporation
Polar	More	Less
Non-polar	Less	More

12. It states that at equilibrium, if a system is subjected to change in any of the factors such as, temperature, pressure, concentration etc, then equilibrium will shift itself in that direction in which the effect of change is reduced.

13. (*b*) *Refer Chapter-5 Solved Example 21 (Ans. 10)*

16. (*b*) The electronic configuration of Na is [Ne] $3s^1$ and that of Mg is [Ne] $3s^2$. The configuration of Mg is more stable (being completely filled) than of Na. Therefore, first ionization enthalpy of Mg is more than that of Na. After the loss of an electron from Na, it acquires the electronic configuration of noble gas, Ne, *i.e.*, $1s^2 2s^2 2p^6$. On the other hand, in case of Mg atom, the electronic configuration becomes [Ne] $3s^1$. Thus, the electronic configuration of Na^+ is more stable than Mg^+ and hence the second ionization enthalpy of Na is much larger than that of Mg.

$$\text{Na}([\text{Ne}]3s^1) \xrightarrow{\text{IE}_1} \text{Na}^+([\text{Ne}]) \xrightarrow{\text{IE}_2} \text{Na}^{2+}(1s^2 2s^2 2p^5)$$

$$\text{Mg}([\text{Ne}]3s^2] \xrightarrow{\text{IE}_1} \text{Mg}^+([\text{Ne}]3s^1) \xrightarrow{\text{IE}_2} \text{Mg}^{2+}([\text{Ne}])$$

$\text{IE}_1(\text{Na}) < \text{IE}_1(\text{Mg})$ $\qquad$ $\text{IE}_2(\text{Na}) > \text{IE}_2(\text{Mg})$

17. (*a*) (*i*) All these ions have same number (10) of electrons. Therefore, these are also called isoelectronic species.

(*ii*) Since the number of electrons are same, the ionic size decreases with increase in nuclear charge. Therefore, the ions can be arranged in increasing order of ionic radii as

$$Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$$

(*b*) (*i*) OCS $\qquad$ (*ii*) NH_3

19. *Refer Chapter-2, Solved Example 26.*

20. *Refer Chapter-6, Solved Example 49 (Ans. –1662 kJ).*

22. *Refer Chapter-7, Solved Example 62.*

(Ans. 5.56×10^{-10}, 7.42×10^{-5}, 8.87)

23. (*b*) *Refer Chapter-7, Solved Example 21.*

(Ans. $[CO_2] = [H_2] = 0.67$ M,

$[CO] = [H_2O] = 0.033$ M)

24. *Refer Chapter-7, Solved Example 101 (Ans. 91.9 times)*

25. *Refer Chapter-1, Solved Exmaple 68.*

Or

Refer Chapter-1, Solved Exmaple 95.

26. *Refer Chapter-2, Solved Example 64.*

27. *(c) Refer Chapter-7, Solved Example 113.*

(Ans. Silver benzoate is 3.32 times more soluble in buffer than in water).

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APPENDICES

A IMPORTANT CONSTANTS & USEFUL CONVERSIONS

B SYMBOLS, FORMULAE AND NOMENCLATURE

LOGARITHM & ANTILOGARITHM TABLES

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Appendix A

IMPORTANT CONSTANTS & USEFUL CONVERSIONS

A : IMPORTANT CONSTANTS

Constant	Symbol	Value
Atomic mass unit	a.m.u.	1.66×10^{-27} kg
Avogadro number	N	6.022×10^{23} mol^{-1}
Electron charge	e	-1.6022×10^{-19} C
Electron mass	m_e	9.1096×10^{-31} kg
		($\approx$ 0.000549 amu)
Faraday constant	F	9.6487×10^{4}C mol^{-1}
		($\approx$ 96500 C)
Gas constant	R	8.314 JK^{-1} mol^{-1}
		0.082 L atm K^{-1} mol^{-1}
Neutron mass	m_n	1.6749×10^{-27} kg
		(1.0087 amu)
Proton mass	m_p	1.6726×10^{-27} kg
		(1.00728 amu)
Planck's constant	h	6.626×10^{-34} Js
Speed of light	c	2.9979×10^{8} m s^{-1}
		($\approx 3.0 \times 10^{8}$ m s^{-1})

B : USEFUL CONVERSIONS

1 Å = 10^{-8} cm = 0.1 nm = 10^{-10} m = 100 pm
1 pm = 10^{-12} m
1 nm = 10^{-9} m
1 atm = 760 mm Hg = 760 torr
1 cal = 4.184 J
= 4.184×10^{7} ergs
1 erg = 2.39×10^{-8} cal
= 10^{-7} J
1 eV = 23.06 kcal mol^{-1}
= 1.602×10^{-19} J
$ln\ x$ = 2.303 log $\boldsymbol{x}$

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Appendix B

SYMBOLS, FORMULAE AND NOMENCLATURE

Symbols

For the sake of convenience, we frequently use abbreviations for lengthy names. *The abbreviations used for the names of the elements are called* **symbols.** In early days, the alchemists used to represent the elements, by using symbols based on astronomical objects. For example, gold was represented by sun, iron by mars and copper by venus. These were not quite significant. The credit of introducing the present system goes to Berzelius a Swedish chemist. He suggested to use the first letter of the name of the element as its symbol. For example, carbon (C), nitrogen (N), oxygen (O), hydrogen (H), boron (B), etc.

However, it was observed that there are many elements, whose names begin with the same letter. Such elements are represented by the first letter followed by some prominent letter of their English names. The first letter of the symbol is capital and the second letter is small. For example, barium (Ba), bismuth (Bi), bromine (Br), beryllium (Be), etc.

In certain cases, the elements are represented by the first letter of the first and some prominent letter of their Latin or German names. For example, potassium (K, derived from Latin name *Kalium*), sodium (Na, derived from Latin name *Natrium*), gold (Au, derived from Latin name *Aurum*).

Radical

Most of the inorganic compounds (acids, bases and salts) are made up of two oppositely charged parts. These positively and negatively charged parts of an inorganic compound are called **radicals**. *The positively charged radical* is called **electropositive** or **basic radical.** The negatively charged radical is called **electronegative** or **acid radical.** For example, sodium chloride (NaCl) consists of sodium (Na^+) as electropositive radical and chloride (Cl^-) as electronegative radical. Similarly, ammonium bromide (NH_4Br) contains ammonium (NH_4^+) as electropositive radical and bromide (Br^-) as an electronegative radical. It may be noted that electropositive radicals are also known as **cations** and electronegative radicals are also known as **anions.**

Common electropositive and electronegative radicals are given in Table 1 and 2 respectively.

Table 1. Common electropositive radicals.

Monovalent	Divalent	Trivalent	Tetravalent
Hydrogen H^+	Cupric Cu^{2+}	Aluminium Al^{3+}	Stannic Sn^{4+}
Sodium Na^+	Barium Ba^{2+}	Ferric Fe^{3+}	Plumbic Pb^{4+}
Potassium K^+	Calcium Ca^{2+}	Chromium Cr^{3+}	Platinum Pt^{4+}
Cuprous Cu^+	Mercuric Hg^{2+}	Auric Au^{3+}	***Pentavalent***
Mercurous Hg^+ or Hg_2^{2+}	Cobalt Co^{2+}	Arseneous As^{3+}	Arsenic As^{5+}
	Stannous Sn^{2+}	Bismuth Bi^{3+}	Antimonic Sb^{5+}

Monovalent	Divalent	Trivalent
Silver Ag^+	Nickel Ni^{2+}	Antimonous Sb^{3+}
Ammonium NH_4^+	Ferrous Fe^{2+}	
Aurous Au^+	Magnesium Mg^{2+}	
	Manganese Mn^{2+}	
	Cadmium Cd^{2+}	
	Strontium Sr^{2+}	
	Zinc Zn^{2+}	
	Plumbous Pb^{2+}	

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Monovalent	Divalent	Trivalent	Tetravalent
Fluoride F^-	Carbonate CO_3^{2-}	Phosphate PO_4^{3-}	Carbide C^{4-}
Chloride Cl^-	Sulphide S^{2-}	Arsenate AsO_4^{3-}	Ferrocyanide $[Fe(CN)_6]^{4-}$
Bromide Br^-	Sulphite SO_3^{2-}	Phosphite PO_3^{3-}	Pyrophosphate $P_2O_7^{4-}$
Iodide I^-	Sulphate SO_4^{2-}	Arsenite AsO_3^{3-}	
Hydride H^-	Thiosulphate $S_2O_3^{2-}$	Borate BO_3^{3-}	
Hydroxide OH^-	Oxide O^{2-}	Phosphide P^{3-}	
Cyanide CN^-	Peroxide O_2^{2-}	Nitride N^{3-}	
Acetate CH_3COO^-	Chromate CrO_4^{2-}	Ferricyanide $[Fe(CN)_6]^{3-}$	
Sulphocyanide or thiocyanate SCN^-	Dichromate $Cr_2O_7^{2-}$	Aluminate AlO_3^{3-}	
Nitrite NO_2^-	Oxalate $C_2O_4^{2-}$	Antimonate SbO_4^{3-}	
Nitrate NO_3^-	Manganate MnO_4^{2-}	Oxychloride OCl^{3-}	
Bisulphide HS^-	Silicate SiO_3^{2-}		
Bisulphite HSO_3^-	Stannite SnO_2^{2-}		
Bisulphate HSO_4^-	Stannate SnO_3^{2-}		
Bicarbonate HCO_3^-			
Chlorate ClO_3^-	Molybdate MoO_4^{2-}		
Bromate BrO_3^-	Plumbate PbO_2^{2-}		
Iodate IO_3^-	Tetrathionate $S_4O_6^{2-}$		
Hypochlorite ClO^-			
Hypobromite BrO^-			
Hypoiodite IO^-			
Hypophosphite $H_2PO_2^-$			
Meta-aluminate AlO_2^-			
Metaborate BO_2^-			
Metaphosphate PO_3^-			
Perchlorate ClO_4^-			
Permanganate MnO_4^-			

Writing the Formula of a Compound

From the knowledge of valencies of various radicals the formulae of chemical compounds can be easily written. The molecules of acids, bases and salts are made up of oppositely charged radicals. The total positive charge on basic radicals is equal to the total negative charge on acid radicals in a molecule. Therefore, in writing the formula of a compound, the positive and negative radicals must be taken in the inverse ratio of their valencies. The various steps involved in writing the formula of a compound are :

Step 1. Write the symbols or formulae of the radical of the compound side by side with basic radical on the left hand side and acid radical on the right hand side.

Step 2. Enclose the compound radical in a bracket.

Step 3. Write the valency of each radical on their right hand top.

Step 4. Reduce the valency numerals to a simple ratio by dividing with a common factor, if any.

Step 5. Criss-cross the valencies, *i.e.* shift the valency numerals crosswise to the lower right corner of the radicals.

Let us apply the above steps in order to write formula of **calcium nitrate.**

Step 1. Writing the formulae of the radicals.

$Ca \qquad NO_3$

Step 2. Enclose the compound radical nitrate in bracket.

$Ca \qquad (NO_3)$

Step 3. Write the valencies of both the radicals on right hand top.

$Ca^2 \qquad (NO_3)^1$

Step 4. Not applicable, because ratio is already simple.

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Step 5. Criss-cross the valencies.

Thus, the formula of calcium nitrate is

$Ca(NO_3)_2$

(*Generally the subscript 1 is not written*)

On the basis of the above steps, the formulae of a few chemical compounds are given below :

Sodium sulphate	Na^1	SO_4^2	Na_2SO_4
Silver sulphide	Ag^1	S^2	Ag_2S
Barium phosphate	Ba^2	PO_4^3	$Ba_3(PO_4)_2$
Calcium oxalate	Ca^2	$C_2O_4^2$	CaC_2O_4
Aluminium nitride	Al^3	N^3	AlN
Sodium borate	Na^1	BO_3^3	Na_3BO_3
Sodium thiosulphate	Na^1	$S_2O_3^2$	$Na_2S_2O_3$

Writing Names of Compounds

During the development of chemistry, many compounds were given common or trivial names. The common examples are H_2O (water), blue vitriol ($CuSO_4 . 5H_2O$), calomel (Hg_2Cl_2), cinnabar (HgS), etc. But later on, these were replaced by systematic names. These are briefly discussed below :

The electrovalent compounds are named by giving the name of electropositive ion first followed by electronegative ion. For example,

KCl	Potassium chloride	K_2SO_4	Potassium sulphate
BaO	Barium oxide	$Ca_3(PO_4)_2$	Calcium phosphate
Na_3AsO_4	Sodium arsenate	$Bi_2(CO_3)_2$	Bismuth carbonate
NiO	Nickel oxide	$K_4[Fe(CN)_6]$	Potassium ferrocyanide

When an element forms more than one oxidation state, the ending - ***ous*** is used to denote lower oxidation state and the ending ***- ic*** is used to denote higher oxidation state. Usually, the Latin names are used for these elements. Recently, it has been suggested to give Roman numerals indicating the oxidation state in brackets following the name of the element. For example,

$FeSO_4$	Ferrous sulphate	or	Iron (II) sulphate
$Fe_2(SO_4)_3$	Ferric sulphate	or	Iron (III) sulphate
Cu_2O	Cuprous oxide	or	Copper (I) oxide
CuO	Cupric oxide	or	Copper (II) oxide
$PbCl_2$	Plumbous chloride	or	Lead (II) chloride
$PbCl_4$	Plumbic chloride	or	Lead (IV) chloride

If two elements form more than one binary compound, prefixes such as *di-* (for 2), *tri-* (for 3), *tetra-* (for 4), *penta-* (for 5), *hexa* (for 6), etc. are used. For example,

SO	Sulphur monoxide	N_2O	Dinitrogen oxide (nitrous oxide)
SO_2	Sulphur dioxide	NO	Nitrogen oxide (nitric oxide)
SO_3	Sulphur trioxide	N_2O_3	Dinitrogen trioxide
		NO_2	Nitrogen dioxide
CO	Carbon monoxide	N_2O_4	Dinitrogen tetroxide
CO_2	Carbon dioxide	N_2O_5	Dinitrogen pentoxide

Simple acids are named by substituting the ending - *ic* for the *-ide* and adding the prefix hydro to the name of the non-metal before the word acid. For example,

HCl	Hydrochloric acid
HBr	Hydrobromic acid
HCN	Hydrocyanic acid.

The oxyacids are named by giving the ending ***-ous*** corresponding to lower oxidation state and ***-ic*** corresponding to higher oxidation state. If there are more than two oxyacids of different oxidation states, the prefixes *hypo-* and *per-* are used. Prefix *hypo-* indicates an oxidation state lower than that of an *-ous* acid while the prefix *per-* indicates oxidation state higher than that of an *-ic acid.* The following are a few examples of common oxyacids :

H_2SO_3	Sulphurous acid	H_2SO_4	Sulphuric acid
HNO_2	Nitrous acid	HNO_3	Nitric acid
HClO	Hypochlorous acid	$HClO_2$	Chlorous acid
$HClO_3$	Chloric acid	$HClO_4$	Perchloric acid
H_3PO_2	Hypophosphorus acid	H_3PO_3	Phosphorus acid

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Equivalent weight of a base $= \dfrac{\text{Molecular weight}}{\text{Acidity}}$

For example,

$NaOH \rightleftharpoons Na^+ + OH^-$ Acidity = 1

Eq. wt. $= \dfrac{\text{Mol. wt.}}{1}$

$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$ Acidity = 2

Eq. wt. $= \dfrac{\text{Mol. wt.}}{2}$

$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$ Acidity = 3

Eq. wt. $= \dfrac{\text{Mol. wt.}}{3}$

Equivalent weight of a salt

The equivalent weight of a salt is that weight of it which contains one equivalent weight of metal.

$$\text{Equivalent weight of salt} = \frac{\text{Mol. wt. of salt}}{\text{Total valency of the metal in the salt}}$$

Appendices

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N	0	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529
18	2553	2577	2601	2625	2648	2672	2695	2618	2742	2765
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

ADD NUMBERS IN MEAN DIFFERENCE COLUMNS

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1	2	3	4	4	5	6	7	8
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

MEANDIFFERENCES

Example : *Log 473.7 = 2.6749 (for 473)*
+ 6 (mean diff. for 7)
2.6755
Mantissa
Characteristic

Log 0.004516 = $\bar{3}$.6542 (for 451)
+ 6 (mean diff. for 6)
$\bar{3}$.6548

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LOGARITHMS

Log_{10}N

N	0	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846
61	7853	7860	7668	7875	7882	7889	7896	7903	7910	7917
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

ADD NUMBERS IN MEAN DIFFERENCE COLUMNS

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0	1	1	2	2	3	3	4	4
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
MEAN DIFFERENCES								

Some Rules

$\log (a) \times (b) = \log a + \log b$ $\qquad$ $\log (a)^n = n \log (a)$

$\log (a) / (b) = \log a - \log b$ $\qquad$ $\ln x = 2.303 \log x$

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ANTI-LOGARITHMS

10^x

x	0	1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2524
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155
x	0	1	2	3	4	5	6	7	8	9

ADD NUMBERS IN MEAN DIFFERENCE COLUMNS

MEAN DIFFERENCES								
1	2	3	4	5	6	7	8	9
0	0	1	1	1	1	2	2	2
0	0	1	1	1	1	2	2	2
0	0	1	1	1	1	2	2	2
0	0	1	1	1	1	2	2	2
0	1	1	1	1	2	2	2	2
0	1	1	1	1	2	2	2	2
0	1	1	1	1	2	2	2	2
0	1	1	1	1	2	2	2	2
0	1	1	1	1	2	2	2	3
0	1	1	1	1	2	2	2	3
0	1	1	1	1	2	2	2	3
0	1	1	1	2	2	2	3

x	0	1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063
.85	7079	7096	7112	7126	7145	7161	7178	7194	7211	7228
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977
x	0	1	2	3	4	5	6	7	8	9

ADD NUMBERS IN MEAN DIFFERENCE COLUMNS

MEAN DIFFERENCES								
1	2	3	4	5	6	7	8	9
1	1	2	3	4	4	5	6	7
1	2	2	3	4	5	5	6	7
1	2	2	3	4	5	5	6	7
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1	3	4	5	7	8	9	11	12
1	3	4	5	7	8	10	11	12
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2	3	5	6	8	9	11	12	14
2	3	5	6	8	9	11	12	14
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2	4	7	9	11	13	15	17	20
2	4	7	9	11	13	16	18	20
2	5	7	9	11	14	16	18	20
1	2	3	4	5	6	7	8	9
MEAN DIFFERENCES								

Example : *Antilog 2.6459 =0.04416 (for .645)*
+ 9 (mean diff. for)
0.004425

A simple rule :

(*i*) If the characteristic is positive, then put the decimal after (n + 1) digits from the left
(*ii*) If the characteristic is negative, then put (n – 1) zeros before the first significant digit

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Useful Relations

$\pi = 3.1416$	$\ln X = 2.303 \log X$	$2.303\ RT/F = 0.05916\ V$
$e = 2.71828$	$2.303\ RT = 5709\ J\ mol$ (at 25°C)	(at 25°C)

Selected Greek letters

α	alpha	ξ	xi
β	beta	ν	nu
γ	gamma	Π, π	pi
Δ, δ	delta	ρ	rho
ε	epsilon	Σ, σ	sigma
η	eta	τ	tau
θ	theta	Φ, ϕ	phi
κ	kappa	χ	chi
Λ, λ	lambda	ψ	psi
μ	mu	Ω, ω	omega

Some Useful Conversion Factors

1 kg	=	1000 gram
1 gram	=	10 decigram
	=	100 centigram
	=	1000 milligram
1 litre	=	$1\ dm^3 = 10^3\ cm^3$
1eV	=	$1.6022 \times 10^{-19}\ J$
1 cal	=	$4.184\ J = 4.184 \times 10^7\ erg$
1 J	=	$10^7\ erg$
1 L. atm	=	$24.217\ cal = 101.32\ J$
1 Å	=	$10^{-8}\ cm = 10^{-10}\ m = 0.1\ nm$
1 atm	=	760 nm Hg
	=	1.013×10^5 pascals
1 bar	=	10^5 pascals

Prefixes

f	p	n	m	m	c	d	k	M
femto	pico	nano	micro	milli	centi	deci	kilo	mega

USEFUL PHYSICAL CONSTANTS

Quantity	Symbol	Value
Speed of light	c	$2.9979 \times 10^8\ m\ s^{-1}$
Atomic mass unit	amu or u	$1.6606 \times 10^{-27}\ kg$
Avogadro constant	N_A	$6.022 \times 10^{23}\ mol^{-1}$
Planck constant	h	$6.6262 \times 10^{-34}\ JK^{-1}$
Faraday constant	F	$9.64846 \times 10^4 C\ mol^{-1}$
Boltzmann constant	k	$1.3807 \times 10^{-23}\ JK^{-1}$
Charge-to-mass ratio of electron	e/m	$1.7588 \times 10^{11}\ C\ kg^{-1}$
Electronic charge	e	$1.60219 \times 10^{-19}\ C$
Gas constant	R	$8.314\ J\ mol^{-1}\ K^{-1}$
Molar volume (STP)	V_m	$22.414 \times 10^{-3}\ m^3\ mol^{-1}$
		$22.414\ dm^3\ mol^{-1}$
Mass of electron	m_e	$9.10953 \times 10^{-31}\ kg$
Mass of proton	m_p	$1.67265 \times 10^{-27}\ kg$
Mass of neutron	m_n	$1.67495 \times 10^{-27}\ kg$
Rydberg constant	R	$1.096 \times 10^7\ m^{-1}$

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